

THE SCIENCE OF METALS

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The maintenance and extension of our industrial and economic civilization depend on the coordinated work of groups of individuals whose efforts are directed toward increase in efficiency, improvement in quality of existing products, and the development of new products. Men who have good character and ability and who in addition have an understanding of human nature are usually selected to guide the activities of these groups. Because these executives direct the expenditure of money and energy, they determine to a large extent the industrial and economic progress of the world. Executives are progressive in proportion to their ability to select men and to stimulate them in obtaining and utilizing fundamental information for the betterment of mankind.

To

BURNIE LEE BENBOW

WHO TYPIFIES THE PROGRESSIVE EXECUTIVE,
THIS BOOK IS DEDICATED.

PREFACE

In the development of the vast complex of products and processes incident to our modern civilization, it is the rule that art precedes science. Man usually learns *how* before he learns *why*. The great variety of metal products now available, and their processes of manufacture, were developed largely by means of endless experiments without the help of general guiding principles. Metals and alloys which have been made and used for thousands of years, have been subjected to scientific study for only about a half century. More and more attention has been devoted to the systematic investigation of the structure and properties of metals and alloys until, at the present time, the rate of accumulation of data is almost too rapid for digestion. We are in possession of a great store of *facts*, in whose assimilation the beginner may well become confused. The need is for a better classification and a more fundamental analysis of this knowledge. It is in the hope of meeting this need, to some extent, that "The Science of Metals" is published.

While the object of the book is thus primarily the exposition of general guiding principles, the material used for illustrative purposes is of a distinctly practical nature. The extent to which the various metals and alloys are discussed is about in proportion to their commercial importance. It is believed that the student of the book will gain a fair acquaintance with the common metals and alloys in addition to an understanding of fundamental principles.

There is no single class of readers to whom the book is addressed. It is hoped that the book will be useful as a text for college students of metallurgical and other branches of engineering, as well as interesting and profitable to those of more experience in the field.

It is a common fallacy to mistake the complex for the profound. It is also quite common to assume that the advanced is difficult. The present treatise is of an advanced nature, in that it presents much of the latest information. It has been our object, however,

to render the treatment not more difficult but more simple. Those portions which have been previously published have been used in a number of colleges for purposes of instruction, and it has been reported that the material is easily understood by the students.

The material in the book has been arranged in logical order from the beginning to the end, with the idea that it will be read in this order. Each chapter therefore assumes an acquaintance with the preceding subject matter. Inasmuch as there will be some who will be interested only in certain subjects, an effort has been made to make each chapter, to some extent, self-contained. This has resulted in a certain amount of repetition. It is believed that this feature will not be found objectionable, since in general the material repeated is of such importance that it will stand repetition.

We wish to express our indebtedness to the Aluminum Company of America and the National Lamp Works of the General Electric Company, in whose laboratories much of the new information presented was obtained. Our thanks are especially due Mr. B. L. Benbow, Manager of the Cleveland Wire Division of the latter company.

We are also indebted to Mr. J. D. Edwards who collaborated on the theory relating to aluminum-silicon alloys, given in Chapter IX, and to Mr. T. J. Doran for the preparation of many of the micrographs and illustrations, as well as to many others who have kindly furnished the micrographs to which their names are appended.

About half of the material in the book has been published in Chemical & Metallurgical Engineering, and the work of Mr. E. E. Thum in editing and criticizing this portion has been of great assistance.

ZAY JEFFRIES.

ROBERT S. ARCHER

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THE SCIENCE OF METALS

CHAPTER I

INTRODUCTORY

Metals have attained such an important place in engineering practice that they have been subjected to much investigation and study, resulting in a wealth of special knowledge. This knowledge is necessary for the most intelligent selection of metals for the varied uses to which they are put, for their proper processing and inspection during manufacture, and, finally, for the development of new and improved metal products.

Cost is Criterion in Selection of Material.—The proper material to select for any given purpose is that which will perform the required service at the lowest ultimate cost. The suitability of the metals for various engineering uses can be predicted with considerable assurance in advance, although actual service is, of course, the final test. Such prediction depends, in part, on mathematical analysis of stresses, but perhaps more largely on comparison with similar conditions of service. In most cases, there are a number of materials which will meet the requirements of the service satisfactorily, and the final selection is based on cost.

Importance of Cost of Processing.—The ultimate cost depends not only on the cost of the raw material, but also on the cost of processing. In a large number of cases where the cost of processing exceeds the cost of the raw material, it is common to find that the cheapest raw material does not yield the cheapest fabricated article. An initial advantage in cost may be more than lost in added cost in machining, cold working, heat treating, or other fabricating operations. The study of metals and alloys from the engineering standpoint must include such considerations.

Quality.—The quality of a metal product is influenced by almost every operation in its manufacture, from melting to the

completion of the finished article. These operations have come more and more under scientific metallurgical control. Melting, casting, hot and cold working, and heat treatment are watched with attention to the quality of the metal as well as to its form. Tests have been devised for application at various stages of manufacture, to insure a satisfactory product. The carrying out of these tests becomes largely a matter of routine, but their development and interpretation require a special knowledge of the structure and properties of metals.

Rôle of Science in Metallurgical Developments.—Metal products which are new in respect to composition or treatment are being developed, that they may better meet existing requirements and the new requirements continually arising. The last two decades have witnessed the development of such materials as high-speed cutting steels, stainless steel, heat-treated machinery steels, a large variety of alloy steels for various special purposes, alloys capable of resisting oxidation at high temperatures, alloys of great strength combined with lightness, and many others which will occur to the reader. These developments have originated largely from accidental discoveries and experimentation of a more or less empirical nature. Art has, as usual, preceded science. The full perfection of the new material thus brought to light has been due, however, in great measure, to the new science of metals. With the further development of metallography and the continued narrowing of the unexplored fields, it is to be expected that science will play an increasingly important part in the development of new metal products.

The Chemical Elements.—There are over 70 chemical elements, of which more than 50 are classed as metals. These elements are characterized by certain properties which have come to be recognized as *metallic*. Some of the most common of these properties are luster, good conductivity for heat and electricity, and, in most metals, the ability to be deformed permanently without rupture. The metals possess these properties in various degrees, and some are decidedly more metallic than others. Arsenic and antimony, for example, while classed as metals, are less metallic than iron and copper. The elements, boron, carbon, and silicon, occupy a position on the border between the metals and the non-metals. They are fairly good conductors of heat and electricity, in which respects they are similar to the metals, but they lack many of the other metallic properties, such

as workability. These three elements are often classed as *metalloids*.

Metals and Alloys.—In a restricted sense, the word “metal” is applied only to the metallic elements. According to common usage, however, a metal is to be defined as any substance having metallic properties. In this broader sense the term includes alloys as well as metallic elements. An *alloy* is a metallic material which is not a chemical element. It may be composed entirely of metallic elements, or of a metallic element in combination with one or more other elements, which may be metals or non-metals. Thus, brass is an alloy of the metallic elements, copper and zinc; bronze is an alloy of copper and tin; while steel is an alloy of the metallic element, iron, with the metalloid, carbon. No metallic substance is known which does not consist chiefly of one or more metallic elements.

Metallography.—Chemical composition may be said to determine the potentialities of an alloy, but not its actual properties. The revolutionary effects of heat treatment and mechanical working on the properties of steel and other alloys are matters of common knowledge. These changes are due to corresponding changes in internal structure. The science of metallography has been defined by Desch as “the study of the internal structure of metals and alloys, and of its relation to their composition, and to their physical and mechanical properties.”

The Structure of Metals.—The application of the microscope to the study of metals has shown that their internal structure is not so homogeneous as might appear to the naked eye. On casual inspection, a piece of metal, such as steel, appears to be a homogeneous substance, like glass, for example. The microscope reveals that even the purest metals, such as pure copper or pure zinc, are complex in structure. The apparently continuous and uniform mass is seen to be an aggregate of crystalline grains. Further examination shows that the properties of the metal are intimately related to the size and shape of these grains. The essence of crystallinity lies in the orderly arrangement of the atoms. It has become possible in recent years, by means of the x-ray spectrometer, to determine the actual arrangement of atoms in crystals and the distances between atom centers.

Atomic Relations in Liquids and Solids.—In the liquid state, the atoms are not arranged in any systematic manner. The forces which tend to fix them into definite crystalline arrange-

TABLE I.—PHYSICAL CONSTANTS OF

Element	Symbol	Atomic weight	Atomic volume	Density, grams per cubic centimeter	Melting point, degrees Centigrade	Boiling point, degrees Centigrade	Linear coefficient of thermal expansion per degree Centigrade $\times 10^{-6}$, 0°–100° C.	Sp. ht., calories per gram per degree Centigrade at room temperature.	Thermal conductivity, calories per centimeter cube per degree Centigrade at room temperature.
Aluminum...	Al	27.0	10.0	2.70	660	1,800	23.1 (25–100° C.)	.21	.48
Antimony...	Sb	120.2	18.0	6.69	630	1,440	10.5	.05	.043
Arsenic...	As	74.96	13.1	5.73	850	360	5.0	.08
Beryllium	Be	9.1	4.9	1.85	1,280
Bismuth...	Bi	209.0	21.4	9.75	271	1,430	13.2	.03	.019
Cadmium...	Cd	112.4	13.0	8.64	320.9	778	31.6	.055	.22
Calcium...	Ca	40.07	26.0	1.54	81016
Carbon...	C	12.005	3,600
Diamond	3.42	3.52	1.18	.11
Graphite	5.35	2.25	7.86	.16	.04
Cerium...	Ce	140.25	20.6	6.79	640045
Chromium...	Cr	52.0	7.5	6.92	1,615	2,200105
Cobalt...	Co	58.97	6.8	8.71	1,444	12.36	.10
Copper...	Cu	63.57	7.15	8.93	1,083	2,310	16.8 (25–100° C.)	.091	.92
Gold...	Au	197.2	10.2	19.32	1,063	13.8 (25–100° C.)	.032	.70
Indium...	In	114.8	15.8	7.28	155057
Iridium	Ir	193.1	8.6	22.42	2,350030	.14
Iron...	Fe	55.84	7.1	7.88	1,530	2,450	11.7	.102	.16
Alpha
Gamma
Lead...	Pb	207.20	18.3	11.34	327.4	1,525	27.09	.030	.083
Lithium	Li	6.94	13.0	0.534	186	1,40083
Magnesium...	Mg	24.32	14.0	1.74	650	1,120	25.8	.24	.38 (0–100° C.)
Manganese	Mn	54.93	7.4	7.42	1,230	1,90011
Mercury...	Hg	200.6	14.7	13.6	–38.87	357.33033	.015 (0° C.)
Molybdenum	Mo	96.0	9.3	10.3	2,625	3,600	5.32 (20° C.)	.063	.35
Nickel...	Ni	58.68	6.7	8.9	1,452	13.2 (25–100° C.)	.102	.14
Osmium	Os	190.9	8.5	22.5	2,700031
Palladium...	Pd	106.7	8.8	12.16	1,550	11.76	.055	.17
Phosphorus...	P	31.04	17.0	1.83	44	290	125.3 (0–40° C.)	.18
Platinum	Pt	195.2	9.1	21.37	1,755	3,910	8.99	.030	.17
Rhodium	Rh	102.9	8.3	12.44	1,950058
Ruthenium	Ru	101.7	8.4	12.06	2,450061
Silicon...	Si	28.1	11.6	2.42	1,420	7.63	.17
Silver	Ag	107.88	10.2	10.53	960.5	1,955	19.21	.054	1.00
Tantalum...	Ta	181.5	10.9	16.6	2,900035	.13
Thorium	Th	232.15	19.1	12.16	1,700028
Tin...	Sn	118.7	10.3	7.3	231.9	2,270	22.96	.053	.15
Titanium	Ti	48.1	10.7	4.5	1,80010
Tungsten	W	184.0	9.5	19.3	3,400	5,830	4.44 (27° C.)	.034	.48
Uranium	U	238.2	12.7	18.7	1,850028
Vanadium	V	51.0	8.5	6.0	1,72011
Zinc...	Zn	65.37	9.1	7.14	419.4	930	29.76	.088	.26
Zirconium	Zr	90.6	14.1	6.4066

THE ALLOY-FORMING ELEMENTS

Electrical resistivity, mil-crohms per centimeter cube	Crystallization shrinkage, per cent.	Young's modulus pounds per sq. inch $\times 10^4$	Latent heat of fusion, calories per gram	Type of crystal lattice	Axial ratio	Lattice constant side of elementary cube or hexagon, A	Closest approach of atoms A ($1A = 10^{-8}$ cm.)
2.83 (20° C.)	6.6	10	77	Face centered cubic.....	4.05		2.86
38.6 (0° C.)	1.4	11		Rhombohedral hexagonal....	2.647	4.28	2.87 3.02
35 (0° C.)							
119 (0° C.)	-3.3	4.6	12.6	Rhombohedral hexagonal. . .	4.54		3.11 3.47
7.54 (18° C.)	4.7	10	13.7	Hexagonal close-packed. . .	1.89	2.96	3.28 2.96
				Face centered cubic.....	5.56		3.03
				Tetrahedral cubic.....	3.56		2.06
				Hexagonal.....	2.75	2.47	1.50
				Hexagonal close-packed, face centered cubic	1.62	3.65 5.12	3.64 3.64
2.6 (0° C.)				Body centered cubic . . .	2.895		2.508
9.7 (20° C.)				Face centered cubic, hexagonal close-packed	1.633	3.554 2.514	2.514 2.514
1.7241 (20° C.)	4.0	17.8	42	Face centered cubic.....	3.60		2.54
2.42 (18° C.)	5.2	11.1	16	Face centered cubic . . .	4.08		2.88
				Face centered tetragonal . .	1.06	4.58	3.33 3.24
6.1 (0° C.)				Face centered cubic.....	3.805		2.69
10.6 (25° C.)		30					
				Body centered cubic	2.86		2.48
				Face centered cubic.....	3.60		2.54
2.04 (0° C.)	3.4		5.4	Face centered cubic	4.92		3.48
				Body centered cubic.....	3.50		3.03
4.35 (0° C.)	4.2	6.25		Hexagonal.....	1.624	3.22	3.22
5							
95.74 (20° C.)	3.75		2.8				
5.5 (27° C.)				Body centered cubic	3.143		2.720
6.93 (20° C.)		30	4.6	Face centered cubic	3.54		2.505
				Hexagonal close-packed . .	1.59	2.714	2.66 2.72
10.2 (0° C.)		13.8	36	Face centered cubic.	3.950		2.795
10.96 (0° C.)		23.5	27	Face centered cubic.....	3.930		2.78
				Face centered cubic	3.820		2.700
				Hexagonal close-packed. . .	1.59	2.686	2.640 2.686
58				Tetrahedral cubic.....	5.43		2.35
1.63 (18° C.)	5.0	10.3	21	Face centered cubic	4.060		2.876
14.6				Body centered cubic.	3.272		2.833
				Face centered cubic.....	5.04		3.54
13.0 (0° C.)	2.8	5.9	14	Body centered tetragonal. .			
3.2				Hexagonal close-packed. . .	1.59	2.97	2.90 2.99
5.6 (20° C.)		60		Body centered cubic.....	3.150		2.726
				Body centered cubic	3.04		2.64
5.75 (0° C.)	6.5	12.4	28	Hexagonal close-packed . . .	1.860	2.670	2.920 2.670
				Hexagonal close-packed. . .	1.59	3.23	3.18 3.24

ments are not sufficient to overcome the motion caused by thermal agitation. On cooling, the energy of motion decreases and, finally, a temperature is reached where the attractive and orienting forces of the atoms gain the ascendancy. Solidification, or freezing, then takes place. This process is identical with crystallization. It is possible to cool some substances from the molten state so rapidly that crystallization does not take place at this temperature. The random arrangement of the atoms may even be preserved until the temperature is so low that the atomic mobility is insufficient to allow crystallization to take place. The substance has then become so viscous as to be a solid. Such solids are said to be *amorphous*. They are really undercooled liquids and their properties are those of very viscous fluids. Pitch, glass, amorphous sulphur, and vitreous silica are common examples of amorphous solids.

The Intergranular Amorphous Cement.—It is not possible, in the case of metals, to prevent crystallization on cooling through the freezing point. There is strong evidence, however, that the structure of the liquid metal is preserved between the crystalline grains in thin films, which, on cooling to atmospheric temperatures, assume the properties of strong amorphous solids. The crystalline grains of a solid metal are, therefore, held together by substantially amorphous metal cement. The metal, as a whole, may be regarded as consisting structurally of two fairly distinct portions, one crystalline and the other amorphous, the latter comprising a very small part of the whole.

Importance of the Atom.—It will be evident from the preceding that the phenomena of crystallization are dependent on the properties of the atom. The atom is the fundamental unit of a chemical element, by which it is differentiated from other chemical elements. Although so small that its size is practically inconceivable to the human mind, the atom is subject to analysis, and conception of its constitution is becoming increasingly definite. It is certain that the study of the atom will, in the future, yield valuable information concerning the properties of metals.

Degrees of Atomic Attraction.—When unlike atoms, that is, atoms of different chemical elements, are brought together, there are three distinct possibilities: (1) The attraction of like atoms for each other may exceed that of unlike atoms for each other. The elements will then fail to combine with each other in any

intimate manner, but will form physically distinct phases. Copper and lead, for example, dissolve in each other in the liquid state only to a very limited extent. In the solid state the extent of their mutual solubility is practically nil. (2) The unlike atoms may have for each other a somewhat greater attraction than the like atoms, but an attraction that is not particularly strong or specific. The elements then form solutions in which the atoms of one kind may be regarded as replaced by atoms of another kind. Such solutions occur in both the liquid and solid states. Copper and nickel are mutually soluble in all proportions in both the liquid and solid states. (3) The unlike atoms may have for each other an attraction of distinctly greater magnitude, exerting itself in a very definite manner. The elements then unite in definite proportions to form chemical compounds. When these compounds crystallize, the relatively great attractions of the atoms for each other contribute to a much greater physical cohesion, manifested by hardness and strength, than is characteristic of the constituent elements. The two soft metals, copper and aluminum, form a compound, CuAl_2 , which is much harder than either of them. Solid solutions are, in comparison, only slightly harder than their constituent elements.

Structure and Properties of Alloys.—Alloys may, therefore, contain, as structural elements or constituents: (1) pure metals; (2) solid solutions; (3) chemical compounds. The quantities of such constituents present, their specific properties, their structural arrangement, and, finally, the nature of the bond between them determine the properties of an alloy.

Definitions and Tables.—Metals are described in terms of a fairly definite set of physical properties which will be referred to so frequently in the course of this book that they should receive some definition and discussion at this point. Table I, on pages 4 and 5, gives the fundamental physical constants of the principal alloy-forming elements. This table should be consulted in connection with the following discussion.

Color.—Metals differ in *color* and in the ease with which they take a polish. Of the pure metals, copper and gold are decidedly yellow, or reddish-yellow. Most of the other metals are white or gray, but may be said to tend toward blue or toward yellow. Robin has arranged some of the common metals in order, ranging from blue toward the yellow as follows:

Zinc (the most bluish).

Antimony.

Lead.

Aluminum.

Iron.

Magnesium.

Tin.

Nickel (the most yellow).

His arrangement is based upon rough rather than polished surfaces. Silver is the whitest of the metals and takes on the most brilliant polish. The metalloid, silicon, is blue-gray in color, while carbon in the form of graphite is black.

Oxidation and Corrosion.—Most of the metals are subject to corrosive attack by the atmosphere and other natural agencies, so that their true colors may not be shown on the natural surfaces. Thus, iron may appear reddish-brown from rust, or a bluish-gray from mill scale. Copper weathers to a peculiar green color, familiar on statuary and other ornamental work of copper and bronze. When copper is heated to about 300° C. in air, its surface becomes coated with a black oxide. This process is made use of in the production of the so-called "gun metal finish." The "blueing" and "browning" of steel articles are also familiar. Gold and platinum are characterized by relative freedom from attack by the ordinary corrosive agencies, and are consequently known as "noble metals."

Specific Gravity and Density.—Most metals are relatively heavy substances. The ratio of the weight of a certain volume of a substance to the weight of an equal volume of water, taken at 4° C., is called its *specific gravity*. In saying that the specific gravity of lead is 11.3, it is meant that lead is 11.3 times as heavy as water at the temperature of 4° C. The *density* of a substance is the mass of a unit volume. If this quantity is expressed in grams per cubic centimeter, the density is numerically equal to specific gravity.

Melting Point and Freezing Point.—When heat is applied to a pure metal in the solid state, a temperature is eventually reached at which fusion abruptly occurs, the metal changing at constant temperature from the solid to the liquid state. This temperature is called the *melting point* of the metal. On cooling the liquid metal, the reverse change takes place, but not necessarily at the same temperature. The metal may remain liquid until it has

cooled some degrees below its melting point. Solidification will then set in rapidly and the temperature of the metal may rise, due to the sudden evolution of heat. The maximum temperature of the metal during the progress of solidification is called the *freezing point* of the metal. Under equilibrium conditions it is identical with the melting point. The melting point of a metal is a physical constant characteristic of the metal. It is affected slightly by pressure, but enormous changes in pressure are required to effect appreciable changes in melting point.

Melting and Freezing of Alloys.—In the case of alloys, the processes of melting and freezing are complex, as will be described in Chap. IX. Melting and freezing usually occur over a range of temperature rather than at a single temperature. The heat given off during the freezing of a metal or alloy, or absorbed during the melting, is called the *heat of crystallization* or the *heat of fusion*. It is expressed in calories per gram.

Vaporization.—All substances exert some vapor pressure, which increases with the temperature. If the vapor pressure becomes equal to atmospheric pressure at any temperature under the melting point, rapid disappearance of the substance by vaporization takes place. This process is called *sublimation*. If the temperature at which the vapor pressure becomes equal to atmospheric pressure lies above the melting point, then the process is called *boiling* and the temperature is known as the *boiling point*. The boiling points of the alloy-forming elements are given in Table I. On account of the experimental difficulties involved, these values do not possess the same degree of accuracy as those for the melting points.

Electrical Properties.—One of the most characteristic properties of metals is their high electrical conductivity, which is far above that of the best conducting aqueous electrolytes or fused salts. Conductivity is the reciprocal of resistivity. The *resistivity* or *specific resistance* of a metal is the resistance of some standard section. The standard section referred to in most scientific work is a block 1 sq. cm. in cross-sectional area by 1 cm. long. The specific resistance is then expressed in microhms per centimeter cube. Other common units for expressing resistivity are:

Microhms per inch—cube.

Ohms per mil—foot.

Ohms per meter—gram.

Since electrical resistivity changes with change in temperature, the temperature of measurement must be given in values for resistivity. The fractional change in resistance for a temperature change of one degree is called the *temperature coefficient of electrical resistance*. In scientific work, this coefficient is based on the Centigrade temperature scale. It is positive for the metals; that is, their resistances increase with increase in temperature. It is negative for carbon, silicon, and boron. The coefficient of resistance is nearly the same for many pure metals, having a value of about 0.004 per degree Centigrade at ordinary temperatures. The coefficient itself changes with change in temperature. It is therefore necessary to specify a temperature or a range of temperature in giving the coefficient.

Thermal Properties.—*Thermal conductivity* is measured in terms of quantity of heat conducted through a section of given area and thickness for a given temperature gradient in a given time. In the c. g. s. system this becomes calories per centimeter—cube per degree Centigrade per second. The ratio of thermal conductivity to electrical conductivity is nearly the same at any given temperature for most of the pure metals.

The *specific heat* of a substance is the quantity of heat required to raise the temperature of unit mass of the substance one degree. In c. g. s. units, it is expressed in calories per gram per degree Centigrade. In English units, this becomes British thermal units (B. t. u.) per pound per degree Fahrenheit.

Most substances expand on being heated. The fractional change in any linear dimension per degree is called the *temperature coefficient of linear expansion*. The Centigrade temperature scale is referred to in the c. g. s. system, while the degree Fahrenheit is the basis in the English system. The fractional change in volume is called the *coefficient of volume or cubical expansion*, and may be taken as three times the coefficient of linear expansion. These coefficients themselves change with temperature.

Mechanical Properties.—The most important properties of metals are those which are broadly and loosely designated as “mechanical properties.” In general, they define the behavior of metals under stress.

Stress.—An external load applied to a body gives rise to a system of internal forces called *stresses*. It is by means of these stresses that one part of the body transmits loads to adjacent parts. Stress is measured in terms of force per unit area.

If a bar having a cross-section area of 2 sq. in. is supporting a load of 5,000 lb., the stress in the bar is 2,500 lb. per square inch. In Great Britain it is common to measure stress in long tons (1 long ton = 2,240 lb.) per square inch. On the Continent the standard is kilograms per square millimeter (1 kg. per square millimeter = 1,422.42 lb. per square inch).

Direction of Stress.—All stresses are fundamentally of the same kind, and can differ only as to intensity and direction. Since intensity is measured in terms of force per unit area, a certain imaginary plane through a body is selected upon which to measure the area over which the total force is acting. The stress tends to produce relative displacement of the two parts of the body on opposite sides of this plane. The direction in which such displacement tends to occur defines the direction factor of the stress. If the two parts tend to be displaced in a perpendicular direction away from the plane of reference, the stress is called a *tensile stress*. If the tendency is to push the two parts toward each other in a direction perpendicular to the plane, the stress is called a *compressive stress*. If the two parts tend to be displaced along the plane, that is, to slide over each other, then the stress is called a *shear*, or a *shearing stress*. Tension and compression are grouped together as *normal stresses*, while shear is a *tangential stress*.

Complex Stresses.—If a plane of reference is taken at random through a body under external load, the stresses on this plane will, in general, be both normal and tangential. In a vertical bar subjected to tensile load, for example, there is on any plane which is neither vertical nor horizontal a component of the applied force tending to cause sliding or displacement along the plane. This results in a shearing stress. On any of these planes there are, then, both tensile and shear stresses.

It is only in the most simple forms of loading that the stress intensity is constant over the entire plane of reference. In a circular shaft subjected to a torsional (twisting) load, the stress on any plane at right angles to the axis is pure shear. The intensity of the stress varies from zero at the axis to a maximum at the periphery.

More often the stress on a given plane varies from point to point both in intensity and direction. Consider, for example, a horizontal beam supported at both ends and loaded at the center. On a vertical plane perpendicular to the axis of the beam

there are both normal and shearing stresses. The normal stress in the upper part of the beam is compression, and in the lower part tension. Regarding compression as a normal stress of negative algebraic sign and tension of positive sign, it can be said that the normal stress varies from a maximum negative value to a maximum positive value. At some zone between the upper and lower surfaces of the beam, the value of the normal stress becomes zero. The line of zero normal stress, which passes through the center of area of the section, is called the *neutral axis* of the section. The intensity of shear stress also varies throughout the section, but reaches a maximum at the neutral axis and is zero at the outer surfaces of the beam.

Summary of Stress Discussion.—To sum up this brief discussion on stress: Stress is made up of forces within a body, usually caused by external loads and tending to produce relative displacements of the constituent parts of the body. Stresses are classified, with reference to any particular plane section of the body, as normal stresses or tangential stresses. If they tend to produce displacements at right angles to the plane, they are normal stresses (tension or compression); if they tend to produce displacements along the plane, they are tangential or shear stresses. On any given plane there may be both normal and shear stresses. These may vary both as to intensity and direction from point to point in the plane. For any form of external loading, the stresses at any point in a body may, within certain limitations, be calculated mathematically.

Deformation.—A condition of stress within a body is accompanied by a change in its external form. This change of form is called *deformation*. When the external load is small, the body regains its original form on removal of the load. The deformation is then said to have been *elastic*. If the load is carried to successively higher values, a point is reached at which the body will no longer regain its initial form on removal of the load. The remaining deformation is called a *permanent deformation*. Removal of the external load does not completely relieve the internal stresses if there has been permanent deformation.

Elastic Deformation.—In metals, the amount of elastic deformation possible is quite small, seldom, if ever, exceeding 1 per cent in a linear dimension. Within such a small range the stress on any given section is practically proportional to the external load, since the area of the section is only very slightly changed

by the deformation. It is characteristic of elastic deformation that the amount of the deformation is, within the limits of accuracy of measurements, proportional to the load, and hence to the stress.

Permanent Deformation.—Permanent deformations may be divided into two classes, according to the mechanism by which they take place. The sluggish deformations of amorphous solids, like pitch or glass, take place in a manner characteristic of fluids, and are called *fluid deformations*. The permanent deformation of metals takes place in a typical way by the sliding of crystal fragments over each other. This type of deformation is called *plastic deformation*. The property of sustaining permanent deformation without rupture is called *plasticity*. Most metals are hardened by plastic deformation carried out at ordinary temperatures. The permanent deformation of a metal at any temperature below its annealing temperature is called *cold working*, and the hardening produced is referred to as *strain-hardening* or *work-hardening*.

Compressibility.—On being subjected to hydrostatic pressure, all substances are reduced in volume. If it is assumed that a piece of metal is perfectly sound physically, that is, free from porosity, then the deformation under hydrostatic pressure will be elastic, up to very high pressures (such as 150,000 lb. per square inch). The changes in volume will be proportional to the pressure. On removal of the pressure, the original volume will be regained, showing the deformation to have been elastic. The ratio of hydrostatic pressure to relative change in volume (during elastic deformation) is called the *compressibility* or *bulk modulus* of the substance. This modulus, E_v , can be calculated from Young's modulus, E , and Poisson's ratio, r .
$$E_v = \frac{E}{3(1 - 2r)}$$
 For $r = 0.30$, $E_v = 0.833 E$.

Young's Modulus.—The most common physical test applied to metals is the tensile test. Under the application of a tensile load, the test specimen elongates. Assuming again a physically sound specimen, this deformation is, in the early stages, elastic. After removal of the load, the specimen will return to its original length. Also, the amount of elastic deformation during the loading is proportional to the load applied. The ratio of normal stress intensity to relative change in length is called the *modulus of elasticity in tension*, or *Young's modulus*. In America it is

expressed in pounds per square inch, while in Great Britain it is expressed in the same units or in long tons per square inch. If the term "modulus of elasticity" is used without any further qualification, it is understood to refer to this quantity. Physically, Young's modulus would be the stress required to produce 100 per cent elongation, but no metal is capable of so much elastic deformation. The modulus of elasticity in compression is practically the same as in tension.

Poisson's Ratio.—During the elastic loading of a tensile test specimen, the diameter decreases as the length increases. The ratio of relative lateral linear constriction to relative change of length is known as *Poisson's ratio*. If the volume of the specimen remained constant, the value of this ratio would be 0.5. Actually, there is a slight increase in volume under tensile loading, and Poisson's ratio has values, different for the various metals, from about 0.24 to 0.42.

Shear Modulus.—The unit deformation produced by a shearing stress is measured by the tangent of the angle of deformation. If a unit cube in the body under stress is imagined, with one face lying in the plane of reference, then the unit shearing deformation is measured by the linear displacement along this face of the cube, divided by the depth of the cube. Just as Young's modulus is obtained by dividing the unit tensile stress by the corresponding unit deformation, so the modulus of elasticity in shear is obtained by dividing the unit shearing stress by the unit shearing deformation. This modulus of elasticity is frequently called the *modulus of rigidity*. It can be calculated directly from Young's modulus and Poisson's ratio.

If E = Young's modulus and r = Poisson's ratio, then the shear modulus, $E_s = \frac{E}{2(1+r)}$. The value of r varies from about 0.24 to 0.42. Assuming an average value of 0.30, $E_s = 0.385 E$.

Proportional and Elastic Limits.—If the tensile loading is continued sufficiently, a point is reached at which the extension of the specimen no longer takes place in an elastic manner. A given increment of load produces a greater increment of extension than in the earlier stages of the test. The extension is no longer proportional to the loading. This point is called the *proportional limit* of the material. Now if the load is removed, it is found that the specimen does not return to its original length, but retains a *permanent set*. The highest stress to which a

material can be loaded without the production of a permanent set is called the *elastic limit*. To the best of present knowledge, elastic limit and proportional limit are fundamentally identical, although slightly different results may be obtained in experimental work. In calculating the elastic limit stress, the load is divided by the original cross-sectional area of the specimen rather than by a reduced area. The amount of the extensions obtained during the elastic loading of metals is so slight that the accurate location of the elastic limit is very difficult. The measured elastic limit decreases as the sensitivity of the measuring instrument or extensometer increases.

Yield Point.—In commercial testing, the true elastic limit is rarely determined. The value which actually is determined is the stress at which an easily perceptible increase in length occurs for a slight increase in load. This value is properly called the *'yield point,'* but is frequently improperly called the elastic limit in commercial testing. It is fairly definite for ductile steels, in which after passing the elastic limit there occurs a considerable extension without appreciable change in load. The yield point is then only slightly above the values which would be obtained for the elastic limit with any ordinary form of extensometer, reading to, say, 0.0001 in. This is not true, however, in the case of most non-ferrous metals, and the term "yield point" does not mean much unless more specifically defined. For general purposes, the yield point may be arbitrarily defined as the stress, calculated on the original cross-sectional area, which produces an elongation of one-half of 1 per cent.

Tensile Strength.—The tensile test is continued until the specimen breaks. The maximum load reached during the test, divided by the original cross-section area of the specimen, is called its *tensile strength*. This value is also variously called *maximum strength*, *ultimate strength*, and *breaking strength*.

Reduction of Area.—When a ductile material like structural steel, for example, is broken in tension, it is found that the specimen is constricted locally at the point of fracture. This is called "necking." The decrease in area at this point, divided by the total original area, is called the *reduction of area* or the *contraction*. It is expressed in per cent. This quantity is apt to vary with the shape of the specimen, being, in general, greatest for circular cylinders.

Elongation.—After rupture, the two ends of the test specimen are fitted together and the total elongation is measured. The relative elongation is expressed in per cent, and is called *elongation*. In giving values of elongation, it is necessary to specify the gage length and the size and shape of the specimen. The necessity for this will be obvious on considering that the cross-section is locally constricted at the point of fracture. It is apparent that the relative elongation will be greatest at this point and will decrease gradually on moving away in either direction. The measured relative elongation will, therefore, decrease as the gage length increases. The elongation will be the same for all test specimens of geometrically similar shape, and nearly the same if equal ratios of gage length to the square root of the cross-section area are maintained. The most common specimen in this country has a cylindrical test section 2 in. in length by 0.5 in. in diameter. (The preferred diameter is 0.505 in., because the area is then practically an even 0.2 sq. in.)

Ductility.—The ability of a material to be permanently deformed without rupture differs according to whether the deformation is brought about by tension or by pressure. *Ductility* is the property by virtue of which a substance may be drawn out in tension without rupture. It involves a combination of plasticity (or fluidity) and tensile strength. There is no definite standard of ductility. It is a property which is expressed in relative terms only. The commonest measures are the elongation and reduction of area of the tensile test, the extent to which a wire can be reduced in section by drawing, and the angle through which a specimen can be bent without rupture. The bend test constitutes the most simple and ready measure of ductility. The actual angle of bend depends, of course, on the size and shape of the specimen and upon the smoothness of its surface. Whereas the plasticity of metals increases, in general, with increase in temperature, the ductility may decrease. The metal may become so weak that it will not sustain the loads necessary for plastic deformation.

Malleability.—*Malleability* is, like ductility, defined in qualitative rather than exact terms. It is the capability of being permanently deformed without rupture by pressure, as by hammering or rolling. It is dependent on plasticity, but is less dependent on strength than is ductility. Malleability, therefore, generally increases with temperature. When a metal is malleable

at ordinary temperatures, but not at high temperatures, it is known as being "red short;" when these relations are reversed, it is said to be "cold short." One measure of malleability is the thinness of sheet which can be produced from a metal by hammering or rolling. The order of malleability for some of the common metals, as given by Fulton, is shown in the table below. For comparison is given his order for ductility, showing that these properties are not exactly parallel. This order refers to the properties at room temperature.

TABLE II

MALLEABILITY	DUCTILITY
1. Gold	Gold
2. Silver	Silver
3. Copper	Platinum
4. Aluminum	Iron
5. Tin	Nickel
6. Platinum	Copper
7. Lead	Aluminum
8. Zinc	Zinc
9. Iron	Tin
10. Nickel	Lead

Resilience.—Deformation requires energy. The work expended is the product of the average force acting, multiplied by the displacement. The work done in elastic deformation is stored up as elastic energy and may be recovered as mechanical work when the load is removed. This elastic energy is the *resilience* of the material. The work expended in deforming unit volume of a material to the elastic limit is called the *modulus of resilience* of the material. It is commonly expressed in inch-pounds per cubic inch.

Toughness and Brittleness.—The total energy or work expended in breaking a material is a measure of its *toughness*. Toughness is not commonly expressed in definite terms. It may be defined as the property of being difficult to break. In general, toughness requires both strength and plasticity. A very deformable substance of low strength, as, for example, a red-hot glass rod, would not be considered tough. On the other hand, a material of high strength but little deformability, like hardened tool steel, is not considered especially tough. *Brittleness* is, in a way, the opposite of toughness. It may be defined as the property of breaking without much permanent deformation. While toughness

depends on both strength and deformability, brittleness involves only the absence of permanent deformability.* A material may be weak and brittle, like burnt steel, or strong and brittle, like good, hardened tool steel. A tough material, however, cannot be weak.

Compression.—The stress-deformation relations in metals under compression are quite analogous to those in tension. The metal deforms, at first, in an elastic manner, as in tension, but with the exception that there is a small decrease in volume, as opposed to a slight volume increase in tension. After the elastic limit is passed, plastic deformation begins. There is, then, this difference, that, whereas plastic deformation in tension reduces the cross-section resisting the applied load, this section is increased by plastic deformation in compression. The load therefore increases more rapidly in compression than in tension.

Failure in Compression.—Failure may take place under compression (1) by secondary shear along a plane at an angle of slightly less than 45 deg. to the direction of the compressive force; (2) by tension at right angles to the compression, which causes splitting along planes parallel to the direction of the compression. The metal may be so plastic that it is practically impossible to cause failure by compression. The compression test is rarely made on metals for the purpose of determining merely the properties of the metal in compression. It is quite often carried out to test the action of a built-up structure, like a column. When a compression test is carried out on small specimens of fabricated metals, such as steel tubing, the quality of the metal is being investigated. Failure takes place by tension or shear, however, and not by compression. The actual measure of quality in such cases is usually the amount of deformation rather than the load.

Torsion.—Metals are very often subjected in practice to torsional loads. A *torsion* load is any load which produces twist. It consists of forces directed perpendicularly to the length of the loaded piece, and not passing through the center of its cross-section. The measure of a torsion load is the twisting moment, which is the product of the applied force by the lever arm or distance from the line of action of the force to the axis of twisting. This quantity is expressed in inch-pounds or foot-pounds. Torsion sets up shear stresses in planes perpendicular to the length of the piece and also in planes parallel to

the length of the piece. Tension stresses are set up at 45 deg. to the shear stresses. The measure of torsional deformation is the angle of twist, and the length along the piece on which this angle is measured. The unit deformation by the shear stresses is not constant through the piece, but varies directly as the distance from the axis of twist. It is expressed for any section by the equation

$$\tan \delta = \frac{\alpha}{L} \times \rho$$

where $\tan \delta$ = unit shearing deformation.

α = angle of twist.

L = length on which α is measured.

ρ = distance from the axis of twist to the section in question.

As long as the loading is elastic, the stress intensity is proportional to the unit deformation and, therefore, to the radius, ρ . After the elastic limit has been passed in the metal furthest from the axis, this relation is no longer true, the actual stress intensity being less than that calculated on the assumption of elasticity. The nominal value of maximum shear stress intensity at failure is called the *modulus of rupture*. This quantity is not a true measure of maximum shear strength, but can be used to calculate the torsion strength of a piece from its dimensions. For ductile materials, the true shear strength is approximately 80 per cent of the modulus of rupture. The quantities determined in a torsion test of a ductile material are yield point in shear, modulus of rupture, modulus of rigidity (shear modulus), and the deformation at break.

Torsion Failure.—Brittle materials subjected to torsion fail by the secondary tensile stresses induced. In the case of a circular shaft, the break occurs along a helicoidal surface. The maximum tensile stress developed is equal to the corresponding shear stress. If the material were elastic up to failure, the modulus of rupture would, therefore, be equal to the tensile strength of the material. Since the proportionality of stress to deformation usually does not hold until failure, even for brittle materials, the calculated modulus of rupture is greater than the tensile strength. The true tensile strength is about 80 per cent of the torsion modulus of rupture.

Hardness.—*Hardness* is one of the most important properties of metals, but there is no universally accepted standard for its

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measurement. It may be defined as resistance to permanent deformation. Different kinds of hardness are distinguished, such as cutting hardness, resistance to abrasion, resistance to indentation, and rebound hardness. There are two standard methods in common use for measuring hardness, and a third method which has been used only to a very limited extent.

The Brinell Hardness Test.—In the *Brinell test* a spherical steel ball, usually 10 mm. in diameter, is pressed into the smooth surface of the specimen to be tested. The measure of the hardness is the ratio of load to the surface area of the indentation. This ratio, expressed in kilograms per square millimeter, is called the Brinell hardness number. The loads used are usually 500, 1,000, or 3,000 kg. The diameter of the indentation, or, more rarely, the depth is measured, and the hardness numbers are obtained from tables furnished with the machines. For very hard materials, the *Brinell test* is inaccurate, because of the distortion produced in the steel ball. This difficulty usually begins when the hardness number reaches about 450 or 500. This is about the hardness of a hardened and tempered automobile transmission gear, for example. In spite of this objection, the *Brinell test* is used in practice quite regularly on materials giving a nominal hardness up to about 700, such as hardened tool steels. The results are not absolutely accurate, but give information of comparative value. Recently, Shore has carried out accurate *Brinell tests* on materials of very great or "super-hardness" by using a small diamond ball. The extended use of the *Brinell test* in practice is largely due to the fact that when similar materials are being tested, such as heat-treated steels, the *Brinell number* is a fairly accurate indication of the associated properties, such as tensile strength and machineability.

The Shore Scleroscope.—In the *Shore scleroscope*, a small diamond-pointed steel hammer is allowed to fall by its own weight from a fixed height on a flat, smooth surface of the specimen to be tested. The hammer is guided by a glass tube, and the height to which it rebounds after striking the specimen is measured by a graduated scale behind the tube. The graduations constitute an arbitrary scale of hardness numbers, on which hardened tool steel is taken as 100. For testing very soft metals, a hammer giving a higher rebound, called a magnifier hammer, may be used. This gives readings approximately 1.75 times those of the universal hammer. The ratio of *Brinell*

hardness to Shore hardness is fairly constant for metals of a given class. Table III shows ratios for various metals as given by the Shore Instrument and Manufacturing Company.

TABLE III

Tool steel hardened and tempered at 600° F.	6.60
Drill rod as received	6.30
Brass, medium hard (drawn)	5.60
Tool steel (carbon) annealed	5.50
Mild steel, hot-rolled	5.25
Brass, drawn, annealed	5.00
Cast iron	4.60
Mild steel, cold-rolled	4.60
Tin-lead alloy	2.00

Comparing the values of these ratios for hot-rolled and cold-rolled mild steel, it will be seen that the scleroscope gives relatively higher readings on the cold-rolled material. This is characteristic, for the Shore numbers are more representative of the yield point than of the tensile strength. The scleroscope test is one of the most commonly used quantitative tests for hardness.

Scratch Hardness.—The third measure of hardness referred to may be called the *scratch test*. This has been worked out in a quantitative manner in the form of instruments called *sclerometers*. These instruments produce a scratch on the surface of the specimen, usually by a diamond point. The hardness may be measured by the force required to plow a scratch of definite dimensions, or by the dimensions of a scratch plowed with a definite force. Such instruments are not at present used to any extent in commercial testing.

Fatigue.—When a metal is subjected to repeated loading and unloading, it is found that the maximum value of stress required to produce failure is much less than that required in a single loading. If the number of repetitions is large, as in nearly all engineering uses of metals, the maximum stress required to produce failure is often well under the elastic limit of the single loading or “static” test. Special tests have been devised to investigate the properties of metals under repetitions of stress, or *fatigue*. The essential feature of these tests is that the specimen is subjected to a large number of definite cycles of stress. Usually, the cycle consists in a variation from a maximum value of tensile stress to an equal value in compression, both stresses being

produced by transverse loading. The *stress range* is, in this case, equal to twice the maximum tensile stress. The stress may, however, vary in an eccentric manner about zero. In any case, the stress range is equal to the algebraic difference between the maximum and minimum stresses. Having fixed the stress range for a test, the measured quantity is the number of cycles before failure.

It is generally considered necessary to run, on any material to be tested, a series of tests employing different ranges of stress. A curve can then be plotted showing the relation between the stress range and the number of cycles before failure. This curve indicates the safe working stress, or *endurance limit* of the material. H. F. Moore has concluded that, in the case of steels, a specimen will run indefinitely under any stress which does not produce failure in 10,000,000 cycles. This conclusion has been questioned, and the generalization certainly is not true in the case of some non-ferrous metals.

The application of rapidly reversed stresses, below the safe working stress, develops a small quantity of heat and causes a slight rise in the temperature of the metal. As the stress range is increased, there is at first a gradual increase in the temperature of the specimen, but a stress is finally reached where the temperature rises sharply in an unmistakable manner. It has been found that the lowest stress range which produces this decided heating effect corresponds closely with the lowest stress range which produces failure of the specimen. The rise in temperature therefore gives a quick indication of the endurance limit of the material.

Another means of determining the endurance limit quickly depends on the observation of deformation. Suppose a specimen to be subjected to alternating transverse stresses, not as a rotating beam but after the manner of a leaf spring. Suppose a small mirror to be attached to the end of the specimen, and a beam of light to be projected on the mirror so that a spot of light is reflected on a graduated scale. When the specimen is vibrated by the application of the alternating stresses, the spot of light on the scale will become a line whose length is a measure of the amplitude of vibration of the specimen. As the stress is increased, the length of the line of light will increase at first proportionately, but at a certain stress there will be a marked increase in the amplitude of vibration of the specimen. This value of stress

might be called a "dynamic" yield point. It has been found to correspond closely with the endurance limit of the material.

Impact Tests.—In fairly recent years a number of tests, called *impact tests*, have been introduced. These tests were designed to test the action of metals under rapidly applied stress, as distinguished from slowly applied stress. In most cases a notch is cut in one side of the test specimen to localize the fracture. Recent investigation has shown that the shape of the notch plays a much more important part in the test than does the speed of impact. For most metals, the single-blow, notched-bar impact test is practically a test of the effect of cutting a notch in a bend test specimen. The results are measured quantitatively in terms of the energy required to break the test piece. These results are not transferable from one form of notched bar to another. The form of specimen must, therefore, be given in stating the results of impact tests

Since many engineering uses of materials involve repeated impacts, several machines have been designed to test materials under this kind of service. The conditions of the test are expressed arbitrarily in terms of the machine used, and the results are given as the number of blows required to produce failure. The specimen is usually notched in some manner to localize failure.

The repeated impact test is practically a combination of the single-blow, notched-bar test with the fatigue test, and the results can be interpreted in this light. If the blow delivered is sufficient to cause failure after a few repetitions, then the test corresponds closely with the single-blow impact test. Under these conditions a soft tough material, like pure iron, would show up much better than a strong but brittle material, like hardened steel. If conditions are carried to the other extreme, and the blow made so light that the specimen endures millions of repetitions, then the test approaches the ordinary fatigue test. A hard steel would then stand up better than pure iron.

CHAPTER II

ELECTRONS, ATOMS, AND MOLECULES

There is an evident development of metallographic science in the direction of a thorough study of the constitution of matter. The microscope has revealed structures in metals unsuspected by the naked eye, and has made intelligible much of the behavior of metals which was formerly quite mysterious. The range of the microscope is limited, however. It is known in many cases that structural changes are taking place on a scale so minute as to lie beyond the resolving power of the microscope and yet they are producing revolutionary changes in the properties of the metal. Since the study of the structure of metals with the microscope has yielded results of such great practical value, it may be expected that the extension of this study to those details of structure which lie beyond the resolving power of the microscope will result in a corresponding extension of the useful knowledge of metals.

The complete analysis of structure is concerned with the ultimate particles of matter—the electron, atom, and molecule. It is not sufficient merely to recognize that such particles exist, and that the atom is an extremely small particle of matter which is the unit of chemical combination. Some appreciation must be gained of the actual sizes of these particles, of their properties, and their relations with one another. In this way a mental picture can be formed of the manner in which metals are built up and of the mechanism of the changes in structure and properties which affect their utility. The knowledge which is now available of the ultimate particles is not enough to make pictures complete and accurate, but it is enough to make them useful.

Constitution of Atoms.—The electron has the smallest mass of any particle of which we have any knowledge. The word “electron” was first suggested in 1891 by Dr. G. Johnstone Stoney as a name for the natural unit of electricity, or a unit electrical charge (4.77×10^{-10} electrostatic units). It is now almost universally applied to certain very small particles which

possess a definite mass and carry a single negative electric charge. It is quite possible that the mass of the particle is entirely of electrical origin, and that the unit electrical charge actually constitutes the particle. The mass of the electron is about $\frac{1}{1,700}$ that of the lightest known atom—namely, the atom of hydrogen. Assuming that this mass is entirely of electrical origin, it can be calculated that the radius of the electron is about 2×10^{-13} cm. Experimental evidence shows that the size of the electron is actually of this order of magnitude, which is very small as compared with the diameter of an atom. Because of their negative charges, electrons are to be regarded as repelled by each other and attracted by positive electrical charges.

It is now considered quite certain that atoms are built up of negatively charged electrons grouped about positively charged nuclei.¹ The charge on the nucleus of an atom is exactly balanced by the negative electrons surrounding it, so that the atom, as a whole, is electrically neutral. Independent methods of experiment have estimated the exact number of electrons outside the nuclei of the atoms of the various elements. If the elements are arranged in the order of increasing atomic weight, and numbered consecutively from 1 to 92, with a few omissions, the numbers thus assigned are called the *atomic numbers* of the elements. According to this conception, the atom of each element has a number of electrons outside its nucleus equal to its atomic number; thus hydrogen has 1, helium 2, iron 26 electrons, etc. Fundamentally, different kinds of atoms owe their individuality to their positively charged nuclei; the charge on the nucleus evidently determines the number of electrons which will be held about it by electrostatic attraction. These electrons will naturally group themselves into some most stable arrangement, which must be different for different numbers of electrons. Atoms of the various elements differ, therefore, in the character of their nuclei, and the number and arrangement of electrons.

Atomic Mass and Volume.—The mass of an atom is due almost entirely to its nucleus. A hydrogen atom contains only 1 electron, having a mass approximately only $\frac{1}{1,700}$ that of the atom,

¹ Langmuir and Lewis have developed a general hypothesis regarding the positions of electrons in atoms and molecules which promises to be very far-reaching. For a clear exposition of this theory see "The Arrangement of Electrons in Atoms and Molecules," *J. Am. Chem. Soc.*, June, 1919.

while the atom of uranium, which contains 92 electrons, has a mass about 236 times that of the hydrogen atom. In the latter case the contribution of the negative electrons outside the nucleus to the total mass is still more insignificant. The total mass of the atom increases with the charge on the positive nucleus, but not in a perfectly regular manner.

The actual mass of the hydrogen atom has been determined and has a value of 1.662×10^{-24} g.; its atomic weight is 1.008. If a hypothetical element with an atomic weight of unity is imagined, the mass of its atom would be 1.643×10^{-24} g. The actual mass of the atom of any chemical element is the product of its atomic weight by the mass of this hypothetical atom. For example, the mass of an iron atom = $55.84 \times 1.643 \times 10^{-24} = 9.175 \times 10^{-23}$ g.

The size of an electron is known to be very small as compared with the volume dominated by the atom of which it is a part.¹ The radius of the latter volume is probably of the order of 50,000 times the radius of the electron. It is believed that the heavy positively charged nucleus of the atom is still smaller than the electron. An atom consists, therefore, chiefly of empty space. It is possible to project one atom through another without striking the nucleus or any of the electrons, in much the same way that a comet might shoot through the solar system, without striking the sun or any of the planets.

In view of the open nature of its structure, an atom cannot be said to possess a definite volume, in the sense of a space enclosed by a bounding surface, but in any given material the volume per atom can be determined, which may, for convenience, be called the volume of the atom, always recognizing that merely the volume dominated by the atom, or its "sphere of influence" is meant. In this sense, it is quite simple to calculate the volume of an atom from its mass and the density of the element. Taking iron again for an example, the density is 7.87 g. per cubic centi-

meter. The number of atoms in 1 c.c. is, then, $\frac{7.87}{9.175 \times 10^{-23}}$; the reciprocal of this number is the volume per atom, and figures 1.166×10^{-23} c.c. This calculation depends, of course, on the value taken for the density of iron, which varies with the temperature, pressure, and arrangement of the atoms—i.e., physical form. Therefore, the volume of an atom, in this sense, is not a constant property of the atom, like its mass. A set of numbers represent-

¹ MILLIKEN, R. A., "The Electron," Chicago University Press.

ing the relative volumes occupied by atoms is obtained by dividing the atomic weights of the elements by their densities when in the solid state. Physically, the number thus obtained gives the volume in cubic centimeters of an atomic weight in grams (gram-atom) of the solid element, and is called the *atomic volume* of the element.

Visualizing the Size of Atoms.—It is difficult to imagine the size of such small objects as atoms. Tungsten, for example, which has a specific gravity of slightly over 19, requires about 100,000,000 atoms, as they are normally spaced at room temperature, to make a linear inch. A 1-in. cube of tungsten would, therefore, contain about 1,000,000,000,000,000,000,000, or (10^{24}) atoms.

In daily life, people are in the habit of visualizing all objects in terms of things which can be seen with the unaided eye—*e.g.*, a map is made of as large an area as the continent of North America, and reduces it to such an extent that its general geographical characteristics can be seen on one page, or one map. On the other hand, objects too small to be seen with the unaided eye are magnified to such an extent that the photograph or other physical likeness can be seen with the unaided eye. The size of an atom cannot be visualized, owing to its smallness, but some idea can be gained of the ratio between atomic dimensions and one of the smallest units which can be readily seen with the unaided eye—namely, 0.01 in. Suppose that, instead of atoms, spheres 0.01 in. in diameter are considered. Further suppose that a cube is made up, composed of 10^{24} of these spheres closely packed. This cube would be 1,000,000 in. on a side, or over 15 miles. Consequently, the diameter of a tungsten atom is to 1 in. as 0.01 in. is to 15 miles, and the space dominated by a tungsten atom is to 0.000001 cu. in. as 0.000001 cu. in. is to 3,375 cubic miles. This comparison may be equally difficult to comprehend, but it at least calls strikingly to one's attention the very small dimensions of the atoms.

Interatomic Forces.—Atoms exert upon each other both attractive and repulsive forces. Thus, metallic iron is an aggregate of crystals built up of atoms arranged in a definite manner, and any attempt to separate these atoms from each other, as by the application of a tensile load, is opposed by the cohesion of the metal, which results from the attraction of the atoms for each other. If a small tensile load, such as 3,000 lb. per square

inch, is applied, the distances between atom centers in the direction of the load increase by a certain amount in accordance with the elastic modulus—in the case in point, 0.01 per cent. On removal of the load, the atoms return to their original positions.

Similarly, the atoms are moved closer together by hydrostatic pressure, resisting the pressure because of the repulsive forces between them. When the pressure is released, these forces restore the atoms to their original positions.

Atoms of a solid are thus held in equilibrium positions by a balance of their forces of attraction and repulsion. On being forced closer together, the repulsive forces increase more rapidly than the attractive forces, and the resultant force is a repulsion which varies approximately as the displacement of the atoms from their equilibrium positions. When the atoms are pulled farther apart than their equilibrium positions, the resultant force is attractive and again is approximately proportional to the displacement of the atoms from their equilibrium positions.

At all temperatures above absolute zero the atoms of the solid elements are in a state of vibratory motion about their equilibrium positions. The frequency of vibration is on the order of 6×10^{12} cycles per second, and does not vary greatly with the temperature; the amplitude of vibration does increase with the temperature, however, thereby increasing the kinetic energy of the particles. In fact, *temperature* is a term used to indicate the mean kinetic energy of the particles of a body.

All of the common properties of a body change with the temperature, except the mass. This must be due to the changing motion and energy of the atoms, since the specific properties of the atom itself do not appear to be affected by temperature. The property of radioactivity, for example, seems to be a characteristic property of certain atoms and does not vary with temperature. Similarly, the spectra of the elements exhibit an independence of temperature, again indicating constancy in the properties of the atom.

The phenomenon of crystallinity is evidence of a natural orderly arrangement of atoms. A crystal is made up of atoms held together by attractive forces which must necessarily be exerted in definite directions to give rise to the geometrical symmetry of the crystal. No element is known which does not occur in crystalline form, both in the pure state and in chemical combination with other elements. The x-ray spectrometer is

constantly giving proof that many substances, once considered amorphous, are in reality crystalline and are built up of atoms arranged in definite and repeating patterns.

This property of exerting force *directionally* is, therefore, a characteristic property of atoms and, because of the directional quality of the forces between atoms, the crystalline form is the normal form of matter in the solid state.

Molecules.—Certain groups of atoms held together by atomic forces constitute molecules. Hydrogen, for example, consists of discrete particles, called molecules, each one made up of 2 hydrogen atoms. Hydrogen in the atomic state is an extremely active substance, combining with explosive violence with many elements, such as oxygen and chlorine. When the atoms of hydrogen unite with each other in pairs to form hydrogen molecules, the attractive forces about the atoms are largely satisfied. Molecular hydrogen is, accordingly, a very inert gas. Hydrogen molecules have little attraction for each other, as is shown by the very low boiling point of liquid hydrogen. It can be mixed with oxygen at ordinary temperatures without any reaction taking place. But when the mixture is heated, some of the molecules are dissociated by the thermal impacts, and the atoms thus freed start the chemical reaction. The heat liberated continues the process of dissociation, so that the reaction rapidly becomes complete.

Equal volumes of gases under similar conditions of temperature and pressure contain equal numbers of molecules (Avogadro's law). From this law the number of atoms to the molecule of a gas can be determined by measuring the density of the gas under definite conditions of temperature and pressure. Such measurements show that the molecules of the non-metallic elements in the gaseous form contain 2 or more atoms, with the exception of the inert gases of the helium group, which are monatomic. Atoms of the rare gases apparently do not exert sufficient attractive force to combine into molecules. Vapors of the metals also contain only 1 atom to the molecule.

Atoms of such elements as oxygen and chlorine exert upon each other definite attractive forces which cause them to unite in pairs to form fairly inert molecules. These molecules, as long as they are undissociated, behave very much like the atoms of the rare gases. The attractive forces of the atoms are so nearly satisfied by their combination with each other that the molecules

do not condense to form liquids, until low temperatures are reached.

Molecules of such chemical compounds as exist in the gaseous state must, of course, contain 2 or more atoms. As a rule, the molecular formula is the simplest that can be written—that is, the molecule contains only one atom of that element which is present in the lowest atomic concentration. Molecular formulas of water vapor and hydrochloric acid, for example, are H_2O and HCl , instead of some multiple, such as H_4O_2 or H_2Cl_2 . The attractive forces which make the atoms of these elements, hydrogen, oxygen, and chlorine, unstable and disposed to double up in pairs are satisfied by the chemical combination with each other.

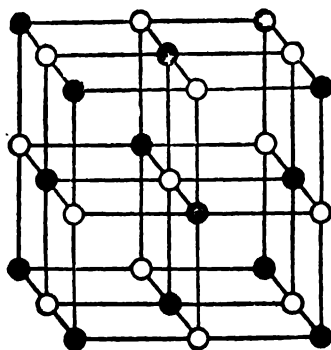


FIG. 1.—Arrangement of atoms in sodium chloride crystal. Simple cubic arrangement.

In Fig. 1 is shown schematically the arrangement of the sodium and chlorine atoms in a crystal of sodium chloride, as determined by the *x*-ray spectrometer. Each sodium atom, represented by a black circle, is surrounded by 6 equidistant chlorine atoms, represented by white circles. Similarly, each chlorine atom is surrounded by 6 equidistant sodium atoms. If solid sodium chloride is heated sufficiently, evaporation takes place, the atoms leaving the surface in pairs in the form of sodium chloride molecules. It is evidently not possible to say which of six similarly related chlorine atoms will pair off with any particular sodium atom in the process of evaporation. The molecule of sodium chloride does not exist, as such, in the solid state.

In sulphur crystals, the atoms are found to be arranged in a lattice structure in groups of 8. It is significant that these groups

contain the same number of atoms as are found in the molecules of sulphur vapor. It seems certain that these groups of 8 atoms must retain their identity throughout the changes of melting and boiling.

From the two examples just given, it is apparent that the definition of a molecule in the solid state is difficult. In many substances like sodium chloride there is apparently no unit which can be called a molecule, unless the whole crystal is called a molecule. Metallic elements all fall in this class. On the other hand, in sulphur and in a large number of chemical compounds, the solid crystal contains certain groups of atoms which may be regarded as molecules.

Chemical Forces.—It has been customary to distinguish rather sharply between the chemical force called "affinity" and the physical forces of cohesion, adhesion, surface tension, etc. On considering the structure of the sodium chloride crystal, it is evident that the forces which are responsible for the cohesion of the crystal are the chemical forces, or the "affinity" between the sodium and the chlorine atoms. This is merely one example of a large mass of evidence which is forcing chemists to the conclusion that the physical and chemical forces between atoms are of the same nature and that there is no justification for a sharp distinction between them.¹

The chemical forces which hold atoms together in the form of distinct molecules are very definite in respect to the number of atoms held in combination. An atom's combining capacity is expressed by the term *valence*. Hydrogen possesses unit combining capacity; it is always held to have a valence of 1. Furthermore, the valence of hydrogen is considered to be positive, while that of the elements with which it combines is considered to be negative, at least in respect to hydrogen. Any element which can replace hydrogen in its compounds is also said to have a positive combining capacity. Oxygen is the standard for negative valence, having a combining capacity of 2, since 1 atom of oxygen combines with 2 atoms of hydrogen. These are simply the ordinary rules of valence, into which it is not necessary to go at further length here.

Simple molecules formed in accordance with these rules often combine with one another to form more complex compounds;

¹ LANGMUIR, IRVING, The Constitution and Fundamental Properties of Solids and Liquids, *J. Am. Chem. Soc.*, 1916 and 1917.

typical examples are hydrated salts and silicates. The numbers of molecules of each kind involved in these combinations are quite definite, but are not indicated by the ordinary rules of valence. There is nothing in the valence of the elements to account for the number of molecules of water in definite hydrates, as $\text{NaCl} \cdot 2\text{H}_2\text{O}$; $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; $2\text{FeCl}_3 \cdot 12\text{H}_2\text{O}$; $2\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$; $2\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$; and $2\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$. Ferric chloride forms a number of distinct hydrates, an illustration of a general tendency for molecules to combine with each other in several different ratios, each definite but apparently unrelated to the valences of the constituent elements or to each other.

Compounds of this type are usually limited to the solid state. Any attempt to volatilize a hydrated salt results in the decomposition of the compound, the water molecules and the salt molecules leaving the solid separately. There is no such thing as a distinct molecule of the hydrate itself, consisting of a definite number of atoms. The "molecule" in the solid state is the entire crystal, which is built up of its simple constituent molecules arranged in definite space lattices. The numbers of the different kinds of molecules which combine with each other in such arrangements depend upon geometrical considerations and not upon any definite combining capacity or valence characteristic of each molecule.

Primary and Secondary Valence.—The forces which cause atoms to combine in definite proportions to form distinct molecules may, for convenience, be termed *primary valence*, and the forces which unite these molecules into crystalline aggregates may be called *secondary valence*, or *residual valence*.

Secondary valence forces may serve to unite like molecules as well as unlike molecules. Thus, ice is built up of H_2O molecules. Two atoms of hydrogen are held to one oxygen atom in this group by primary valence. These molecules are then united by secondary valence in the crystal of ice. Ice is here not regarded as a distinct chemical compound, but merely as a different form of water; its formation from H_2O molecules is, however, a phenomenon of the same type as the formation of crystals of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ from NaCl and H_2O molecules. The forces are equally chemical in nature.

Molecules of the elements are primary valence compounds. The valence of an element toward other elements does not show how many atoms combine to form the molecule, but other

considerations make it possible to classify the forces involved as primary valence forces. The very existence of the molecule as a discrete particle passing probably unchanged through solid, liquid, and gaseous states is typical of a primary valence compound. The heat of formation of molecules from like atoms is of the same order of magnitude as in the case of molecules formed from unlike atoms—that is, chemical compounds. The heat of formation of molecular hydrogen from atomic hydrogen, for example, is about 80,000 cal. per gram-molecule. Heat evolved in reactions due to secondary valence is, in general, very much smaller and corresponds in magnitude with heats of fusion and evaporation.

Elements in the solid state are normally crystalline aggregates of the molecules of which they are constituted when in the gaseous state. Sulphur crystals are built up of molecules containing 8 atoms each. Metallic elements are, as far as is known, mon-atomic in the gaseous state; *accordingly, the unit of which crystals of solid metals are constituted is the atom.* The forces holding these atoms together are similar in kind to those uniting the molecules of sulphur in crystalline sulphur and the molecules of water in ice, the forces of secondary or residual valence.

Compounds between Metals.—Metals frequently form definite chemical compounds which are important structural constituents in alloys. It is a conspicuous characteristic of these compounds that their compositions are seldom indicated by the rules of primary valence. Probably the most important compounds of this class are Fe_3C and CuAl_2 . It is, of course, possible to write structural formulas after the manner of organic chemistry, in which the ordinary rules of valence are satisfied. Thus, the con-

$$\begin{array}{c} \text{Cu} \\ \diagup \quad \diagdown \\ \text{Al} = \text{Al} \end{array}$$

stitution of CuAl_2 might be represented by the formula, $\text{Al} = \text{Al}$. This would indicate that the crystals of this compound are built of molecules as units in the space lattice. It is probable that such is not the case, but that the units of the crystal lattice are the atoms of copper and aluminum arranged in definite and repeating patterns, in which the atoms of copper and aluminum are not interchangeable. Since atoms of a pure metal do not combine with each other to form molecules, it seems quite likely that the atoms of two metals, which though different are nevertheless of generally similar chemical characteristics, likewise

do not form primary valence molecules. Neither is the formation of intermetallic compounds accompanied by the large heat evolutions which so often accompany primary valence reactions. Furthermore, no intermetallic compounds are known to exist in the gaseous state, except for such feebly metallic compounds as the hydrides of antimony, arsenic, and bismuth. These hydrides are composed of discrete molecules, whose constitution is represented satisfactorily by the simplest possible formula based on the ordinary rules of valence. Therefore, the majority of intermetallic compounds seem to be secondary valence compounds, whose compositions are determined by geometrical considerations, such as the sizes of the atoms and the directional properties of their force fields, just as in the case of the hydrates discussed above.

Mechanism of Solidification.—Liquids as well as solids must be held together by secondary valence forces. Gases consist of molecules in such a violent state of thermal agitation that the attractive forces between them are not strong enough to cause even temporary combinations. In the liquid state the energy of thermal agitation has decreased to such an extent that the collisions between molecules result in the formation of groups held together by secondary valence. Further collisions break up these groups so that their existence is only temporary and, in actual time, extremely brief. Liquids owe their fluidity to this constant shifting in the bonds between molecules. As the temperature is further lowered, the life of these molecular groups and the average number of molecules in them increase. Finally, a point is reached at which the thermal energy of the individual molecules is not great enough to free them from the attraction of other molecules, and solidification takes place. The expansion which takes place when water cools from 4° to 0° C. suggests the formation in the liquid of considerable molecular groups having the increased volume characteristic of crystalline ice. The metal bismuth also expands on solidification, and a slight expansion of the liquid immediately before solidification would be expected, as in the case of water, or at least a decrease in the rate of fluid contraction.

The constriction of thermal motion can be accomplished by an increase in external pressure as well as by a decrease in temperature. If solidification takes place with a decrease in volume, as is the case with all the common metals except bismuth, the application of external pressure hastens solidification—that is,

causes it to take place at a higher temperature. When solidification is accompanied by expansion, increase in pressure lowers the freezing point, but the actual changes in freezing point caused by changes in pressure are very slight.

This discussion may be reviewed by the consideration of an example. Suppose some metallic tin is heated to a temperature of $2,500^{\circ}\text{C}$. Under normal atmospheric pressure the tin will be in the gaseous state, since it boils at about $2,270^{\circ}\text{C}$. To the best of knowledge, the gas is monatomic—that is, the molecules consist of single atoms. These atoms are in constant motion in straight lines, interrupted only by collisions. Each atom is surrounded by a field of force which attracts it to the other atoms with the same intensity as in the solid state. The kinetic energy, both of translation and rotation, overcomes the attractive forces, and no combination of atoms takes place. On cooling, this kinetic energy decreases until the attractive forces sufficiently overbalance it to cause the condensation of the gas to a liquid. Since the volume change is very much greater on passing from the gaseous to the liquid state than on passing from the liquid to the solid state, the effect of pressure on the boiling point is very much more marked than on the melting point. In liquid tin, the atoms are held together by cohesion bonds of the secondary valence type, constantly breaking and re-forming, so that the positions of the atoms with reference to one another are not fixed. The liquid is, therefore, mobile, and can change its shape indefinitely without losing its continuity.

The atoms of tin are constantly tending to orient themselves into a regular pattern, a tendency which is opposed by the energy of thermal motion. When this energy is sufficiently reduced, by cooling to 232°C ., the orienting or crystallizing tendency gains the ascendancy and solidification takes place. Solidification is identical with crystallization, or the arrangement of atoms into positions fixed with relation to each other. The atoms remain in a state of vibration about their equilibrium positions, but have probably lost their energy of rotation. On further cooling, the amplitude of vibration decreases, causing a contraction of the metal. As the kinetic energy of the atoms decreases and they become closer together, it requires a greater external force to separate them—that is, the cohesion increases.

Crystals which form on solidification grow outward from nuclei until they meet each other along surfaces which are neces-

sarily irregular. Some of the molten tin remains between the crystals in an unoriented or amorphous condition. On cooling to room temperature, the motion of the atoms of the amorphous metal decreases to such an extent that the material, although possessing many of the structural features of a liquid, becomes rigid and is, in effect, a solid. However, the atoms retain their ability to change their position with relation to one another, and the substance is, therefore, capable of flow. Transition from a liquid to an amorphous solid is gradual, and there is no sharp freezing point and no heat of solidification; an amorphous solid is doubtless an undercooled liquid.

Compression.—T. W. Richards¹ has pointed out that the attractive forces between atoms act in many ways like the application of external pressure. "There is strong evidence that where affinities are great the atomic centers come closer together, and that where the affinities are slight they are further apart." Richards considers the atom as including the entire "sphere of influence," or space dominated by the atom. On this basis, atoms must necessarily be regarded as compressible, in order to account for the compressibility, expansibility, etc., of solids. The volume of an atom is, then, a definite quantity, depending on the pressure to which it is subjected.

This pressure may arise from external forces or from interatomic attraction. In the latter case, it is spoken of as an internal pressure, and substances held together by strong affinities are said to be under high internal pressure. A striking example of compression by chemical affinity is found in the case of potassium chloride. The atomic volume of potassium is 45 (cubic centimeters per gram-atom) and the molecular volume of KCl is 37 (cubic centimeters per gram-molecule). In the compound the potassium atom and the chlorine atom together occupy less space than does the potassium atom alone in solid metallic potassium. This contraction is held to be due to a high internal pressure caused by the strong affinity of potassium for chlorine.

Small atomic volume is thus evidence of high internal pressure, which should be accompanied by great cohesion. The same forces that resist the separation of atoms by mechanical tension also resist their separation by thermal agitation; therefore small atomic volume should, in general, indicate low coefficient of

¹ RICHARDS, THEODORE W., The Present Aspect of the Hypothesis of Compressible Atoms, *J. Am. Chem. Soc.*, Dec., 1914.

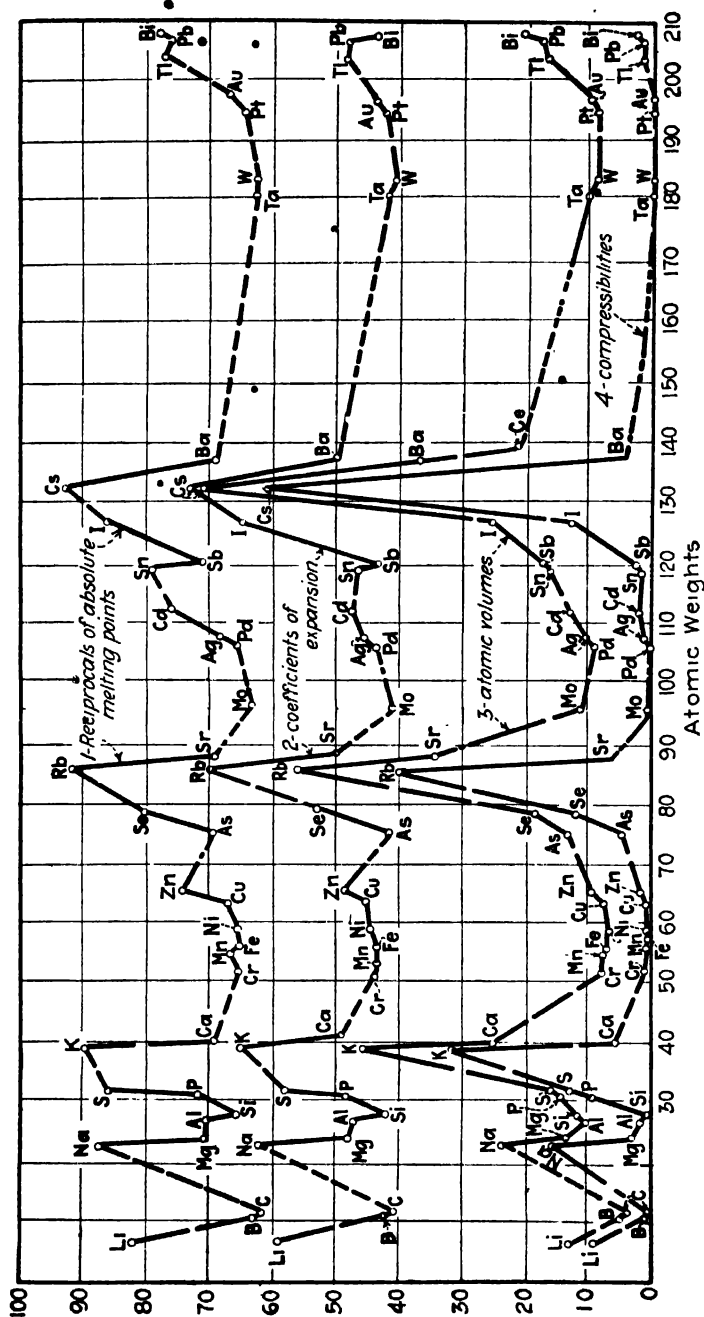


Fig. 2.—Correlation of fundamental properties of the elements. (Richards.)

thermal expansion, high boiling point, and high heat of vaporization; such assumptions are verified in a most remarkable way in the diagram (Fig. 2)¹ collecting the experimental evidence now available.

The volume of any substance is diminished by the application of hydrostatic pressure. If it is supposed that all solids are inherently under internal pressure, then the actual effect of a given absolute increment of external pressure, such as 1,000 lb. per square inch, must be greater the less the initial internal pressure. The fixed increment of pressure will be effective in proportion to its ratio to the total internal plus external pressure on the substance, and those elements whose internal pressures are low, as shown by high atomic volumes, should have high compressibilities.

Influence of Atomic Volume on the Constancy in Compressibility.—In a system already under great pressure each small successive addition of pressure will be nearly the same percentage of the whole, and therefore each like addition would be expected to have very nearly the same effect upon the volume. On the other hand, if the substance is under small pressure, each successive equal addition of pressure will be a much smaller percentage than the preceding and would, therefore, have a greatly diminished effect upon the volume. Thus, if the compressibility decreases greatly with increasing pressure, one may infer that but little pressure was present in the first case, but if a body possesses a small compressibility which is nearly constant over a wide range of pressure, we should feel obliged to believe that a great internal pressure was already present in some form within the substance.

Accordingly, substances which, like carbon, silicon, iron, etc., possess low atomic volume and low compressibility, should also show considerable constancy in compressibility with varying pressure.

These relations are actually found to hold with considerable regularity in the case of elementary substances, and,

Consistently, elements with great atomic volumes also show, in general, great volatility, great compressibility, great coefficient of expansion, and great change of compressibility with increasing pressure.

¹ From an article by RICHARDS, T. W., The Compressibilities of the Elements and their Relations to Other Properties, *Proc. Nat. Acad. Sci.*, vol. 1, p. 411, July, 1915.

CHAPTER III

THE CRYSTALLINE STRUCTURE OF METALS

Perhaps because, ordinarily, regularity of external form, brittleness, and transparency are associated with the crystalline state, it seems somewhat strange to regard ordinary pieces of metal as crystalline. The essence of crystallinity, however, lies in regularity of internal structure, and it has been abundantly proved that all metals are crystalline. Study of their crystalline structure has led to very clear conceptions of the mechanism of deformation and failure, and to a general theory of the strength of metals and alloys. The application of *x*-ray analysis has made knowledge of crystal structure more complete and exact, and is clearly destined to play an important part in the future development of metallographic science.

Crystallinity depends upon an orderly arrangement of the molecules of a substance. In the molten condition, or in solution in a solvent, the molecules are arranged in a haphazard manner. On the other hand, when the substance crystallizes, the molecules group themselves according to definite and repeating patterns. Metals are monatomic—that is, their molecules contain only one atom. The case under consideration in this chapter is thus simplified, in that the atom is the unit in the pattern.

Space Lattices.—The pattern which forms the foundation upon which a crystal is built is known as a *space lattice*. It consists of a series of points in space, such that every point is situated similarly to every other point. Space may be imagined as divided into cells by three sets of parallel planes. The planes of each set are at equal distances from each other and parallel; the distance between planes may be different in the various systems, and the three sets of planes may form any angles with each other. The points of intersection of these planes constitute a space lattice, as is illustrated in Fig. 3.

The arrangement of atoms in planes is responsible for the characteristic and commonly observed properties of crystals.

For instance, when a crystal is allowed free development, it assumes a form bounded by plane faces. The direction, or orientation, of these faces is determined by the lattice underlying the crystal. Similarly, it is found that crystalline bodies often possess the property of breaking easily along certain planes, called "cleavage planes." Deformation of metals takes place by sliding on planes known as "slip planes," as will be described

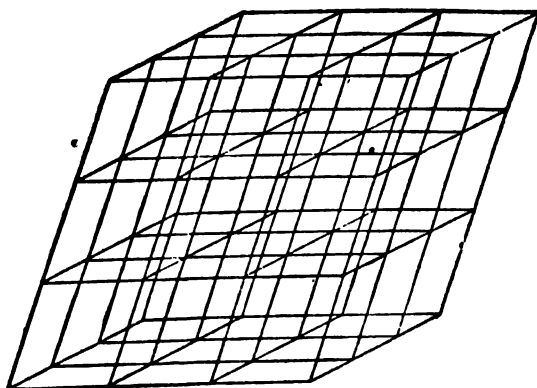


FIG. 3.—Three sets of parallel planes whose intersections form a particular space lattice. (Bragg.)

later. In any given crystal, the orientation of the cleavage planes and slip planes is fixed. When a crystalline substance is subjected to attack by a chemical solvent, it is found that the resistance to solution is greatest on certain planes. The planes determining external form, cleavage, slip, and resistance to chemical attack are planes which pass through atom centers in the space lattice. It will readily be seen that a very large number of sets of parallel planes could be drawn which would pass through all of the atoms, but the significant planes are limited to those on which the concentration of atoms is large.

Symmetry.—Any plane passing through a crystal in such a way that the atoms on one side occupy the positions of mirror images of those on the opposite side is a *plane of symmetry*. Two kinds of planes of symmetry are distinguished. If the structure on one side of the plane can be rotated on the plane through some angle (other than 180 deg.) without destroying the symmetry, the plane is said to be a *principal plane of symmetry*. If such rotation destroys the symmetry for all positions other than the original or one reached after a rotation of 180 deg., then the plane

is called a *secondary plane of symmetry*. To express this more mathematically, principal planes contain two or more equivalent and interchangeable directions, while secondary planes possess no interchangeable directions.

An axis of symmetry is a line through a crystal such that a revolution about it, through some angle less than 360 deg., will result in a duplication of the original position of the crystal. The degree of symmetry with respect to the axis depends on

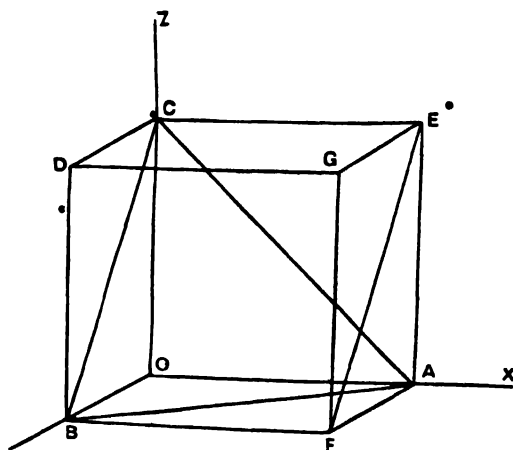


FIG. 4.- Sketch of cubic crystal. (Bragg.)

the number of times during a complete revolution that such duplication occurs. When such a condition is brought about by a revolution of 180 deg., or twice during a complete revolution, the crystal is said to possess a twofold or binary symmetry. Similarly, the classification is extended to threefold or ternary, fourfold or quadratic, and sixfold or hexagonal symmetry. Axes of more than twofold symmetry are called "principal axes of symmetry." Twofold or binary axes are called "secondary axes."

In considering their structural characteristics, crystalline bodies are looked upon as extending indefinitely, in all directions. The planes and axes referred to represent directions rather than specific planes or lines. Other planes through atom centers parallel to a plane of symmetry are likewise planes of symmetry of exactly the same kind. When it is said that the isometric system possesses three principal planes of symmetry, it is meant

that there are three sets of parallel planes, any one of which is a principal plane of symmetry for a crystal extending indefinitely in all directions.

Isometric or Cubic System.—The direction of a crystallographic plane is defined by referring it to a system of axes chosen with respect to the particular crystal system under consideration. The cubic or isometric system, which is the simplest and also the most common among metals, will serve to illustrate the method of designation. Axes OX , OY , and OZ (Fig. 4) are, in this case, the intersections of the three principal planes of symmetry. They are perpendicular to each other and are said to be of equal length, meaning that the same scale is used to represent distances on all the axes, and there is nothing inherent which distinguishes one from the other.

Plane ABC is called the "ground plane." In all systems one of the parameters¹ of the ground plane is taken as unity, for simplicity of reference, and the other parameters are then fixed in accordance with the nature of the system. In the isometric system all of the parameters of the ground plane are equal and hence unity, and plane ABC intersects all axes at equal distances from the origin.

The *indices* of a plane are the reciprocals of the parameters, and planes are more usually designated by indices. The planes noted in Fig. 4 have indices as follows:

ABC	(111)	$CEBF$	(011)
$CDGE$	(001)	$DGBF$	(010)

For the definite designation of each set of parallel planes, the directions of OA , OB , and OC in Fig. 4 are considered positive, and the opposite directions negative. If the parameter of a plane is negative, then the corresponding index is negative, and it is written with the negative sign above the index. If the parameters of a certain plane are $OA = -2$, $OB = 1$, $OC = 1$, the indices are $\bar{1}\bar{2}$, 1, 1. Since, however, indices and parameters express only ratios, not the actual position of a particular plane but the direction of a series of parallel planes, the indices ($\bar{1}\bar{2}$, 1, 1) are the same, crystallographically, as ($\bar{1}$, 2, 2), ($\bar{2}$, 4, 4), etc. Writing without commas, ($\bar{1}22$) is used, because it has no fractions and has at least one index unity. The above system of notation is the Miller system. In metallography, when symmetry permits,

¹ The parameters of any plane are the intercepts on the axes of reference. The parameters of plane $CDGE$, for example, are ∞ , ∞ , and $(OC) = 1$.

the indices are used without signs to represent not only one system of parallel planes but all sets of parallel planes having the same spacings. For example, the 100 planes in the isometric system include all of the cube faces; the 110 planes include all of the cube diagonals, etc.

Crystal Systems.—All possible crystal structures can be divided into six groups, each characterized by a particular grade of symmetry:¹

1. *Isometric or Cubic System.*—Three principal and six secondary planes of symmetry. Crystals referable to three equal rectangular axes. Most metals belong to this system.

2. *Tetragonal System.*—One principal and four secondary planes of symmetry. Crystals referable to three rectangular axes, only two of which are equal. No metals are known to belong to this system, with the exception of tin and indium.

3. *Hexagonal System.*—One principal and six secondary planes of symmetry. Crystals referable to four axes, three of which lie in the same plane intersecting at 120 deg., and are equal in length. The fourth axis is perpendicular to the plane of the three others at their intersection and may have either greater or less length. The metals magnesium, zinc, and cadmium, belong to this system.

There are three other systems—namely, orthorhombic, monoclinic, and triclinic—in which no pure metals are known to crystallize.

Visible Metallic Crystals.—Under some circumstances the crystalline nature of metals becomes apparent to the unaided eye. The crystalline appearance of the zinc on iron galvanized by the hot-dip process is familiar to everyone. Similar regularity of external form is frequently produced when metals solidify with one surface free from restraint. Figure 5 shows the surface of a piece of cast tellurium which solidified in an open mold.

During solidification of a metal, crystallization begins at centers called “nuclei,” and proceeds in a directional manner. Growth is most rapid along some line which bears a simple relation to the symmetry of the crystal. A trunk shoots out in this direction and branches grow out from the sides of the trunk parallel to one another and in directions determined by the structure of the crystal. The result is a formation which, from its resemblance to a tree, is called a *dendrite*. The dendritic appearance of

¹ BAYLEY, W. S., “Elementary Crystallography,” McGraw-Hill Book Co.

many of the crystals can easily be seen in the photograph of tellurium (Fig. 5). Because of the fact that most metals contract on solidifying, the dendrites which form on the surface of a metal are left in relief by the lowering of the level of the liquid metal.

Since several nuclei form simultaneously and growth proceeds in all directions (especially when the nuclei are completely surrounded by the molten metal), it is obvious that adjacent



FIG. 5.—Dendritic crystals on surface of cast tellurium. $\times 1\frac{1}{2}$.

crystals growing toward one another must meet. If a single crystal is allowed to develop from a molten bath, its external shape will be a fairly perfect geometrical figure. With a large number of growing crystals, however, as the molten metal becomes exhausted, the crystals must meet in such a manner as to fill the space completely. These crystals will be oriented in different ways, and hence, in order to fill space, cannot form their habitual external shapes. Such a crystal, with orderly arrangement of the atoms in the interior but an external shape determined by the influence of other crystals, is called an *allotriomorphic crystal*, or *crystallite*, or, more commonly, a *grain*. In any given grain, therefore, the atoms are arranged in the same manner as they would be in a perfect crystal of the metal, but the grain may have any external shape.

No two adjacent grains in a cast metal have the same orientation. By "orientation" is meant the direction of the crystallographic axes. If two adjacent grains had the same orientation, the boundary between them would disappear and the two grains would become one. A metal, therefore, which has solidified from the molten state consists of an aggregate of differently oriented grains. These grains vary widely in size and shape, according to the specific crystallizing properties of the metal itself, the rate of cooling through the solidification range, the temperature gradients, purity, and other factors. Sometimes the grains are so large that they can readily be seen with the unaided eye, and at other times they are so small that a microscope is required to see them.

Etching Polished Sections.—For examination under the microscope, a piece of metal must be ground or filed flat, and then carefully polished. Examination may then reveal no structure whatever, except for particles of included foreign matter, such as slag and oxides. The boundaries of the grains themselves are not distinguishable. It has been suggested by Beilby¹ that the process of polishing has produced a surface layer of amorphous metal which is opaque and covers the crystalline metal underneath. This amorphous layer can be dissolved in a chemical reagent in which the metal is soluble. The process of chemical attack on the polished surface is called *etching*. The boundaries between the grains are regions of low resistance to chemical attack and their location is shown after light etching.

Deeper etching develops marked differences in color between different grains, some appearing dark and others light. The process of solution produces minute facets, which vary in orientation from one grain to another. Light falling on an etched surface will be reflected into the microscope only by such facets as have the appropriate orientation. These grains will appear light, while other grains will appear darker. The different tints of the grains are, therefore, evidence of their crystallinity and of their different orientations.

Still deeper etching often produces within certain grains geometrical figures which are called "etching pits." These pits approximate a definite geometrical form, such as a triangle or rectangle, and within any particular grain have the same form

¹ BEILBY, SIR GEORGE, "The Hard and Soft States in Metals," May lecture, Institute of Metals, 1911.

and orientation. They furnish additional evidence of the crystallinity of metals. . . .



FIG. 6.—Light etching showing grain boundaries in Armco iron. $\times 50$.

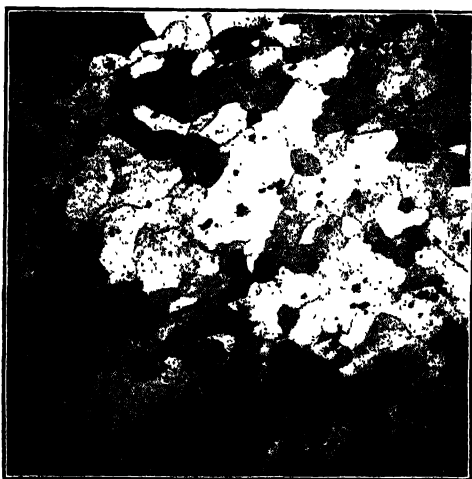


FIG. 7.—Moderate etching showing grains of different tone in Armco iron. $\times 50$.

The various effects of etching just described are shown in Figs. 6, 7 and 8, taken from a specimen of nearly pure iron (Armco iron).

Intracrystalline Slip.—If a piece of ductile metal is polished and etched to bring out the grain boundaries, and is then subjected to a load which causes a slight permanent deformation, examination under the microscope reveals systems of parallel lines running across the grains. In any one grain the lines are approximately straight and parallel to one another, but their direction is different



FIG. 8.—Deep etching showing etching pits in Armco iron. $\times 1,000$.

in different grains. In the first stages of deformation only a few of these lines appear, and not in every grain. As the deformation increases, more lines appear, becoming closer together and appearing in grains previously free from them. Finally other sets of lines are developed, parallel to one another in any one grain and crossing the first set of lines. Close examination shows that the first sets of lines have been displaced along the second sets by a minute amount, so that they no longer register exactly.

The nature of these lines has been very carefully investigated,¹ and they are known to represent block movement or slip along

¹ HOWE, HENRY MARION, "The Metallography of Steel and Cast Iron," McGraw-Hill Book Co.; EWING and ROSENHAIN, "The Crystalline Structure of Metals," *Phil. Trans.*, vol. 195, p. 279; STEAD, "The Crystalline Structure of Iron and Steel," *J. Iron Steel Inst.*, 1898, I, p. 145; ROSENHAIN, WALTER, "Introduction to the Study of Physical Metallurgy," D. Van Nostrand Co.

crystallographic planes. The lines observed are steps on the polished surface produced by the elevation or depression of blocks or fragments of the grains. They are called *slip bands*, and the crystallographic planes along which slip occurs are called *slip planes*. A slip band becomes visible under the microscope only when the displacement along the slip plane is on the order of 0.00001 in., which corresponds roughly to 1,000 atom diameters. Displacements have been measured as high as 0.00005 in., or about 5,000 atom diameters. Even greater movements probably occur in severe deformation.

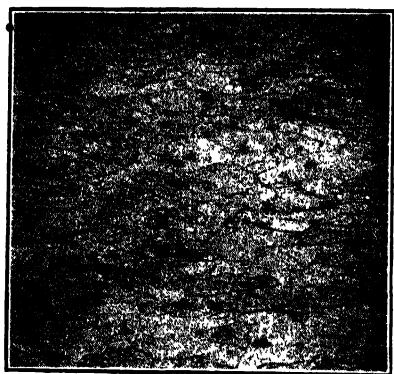


FIG. 9.—Armco iron cold pressed; 60 per cent reduction in thickness. $\times 50$.

Cold Work or Plastic Deformation.—The great permanent deformations imposed on metals in the various processes of mechanical working, such as rolling, forging, and drawing, are substantially integrations of very many block movements along slip planes. This type of deformation is called “plastic deformation,” as opposed to “fluid deformation,” which is characteristic of liquids and of amorphous solids like pitch and glass. In plastic deformation, relative motion is confined to the slip planes, the crystalline fragments between such planes moving as units in which the atoms retain substantially their initial relative positions with respect to their neighbors.

When the external shape of a piece of metal is changed by a deforming load, the shapes of the grains undergo similar changes. Normally, the grains are so shaped that, on the average, their diameters are equal in all directions. Such grains are called “equiaxed grains.” Now if the metal is deformed, as by drawing

out into a wire, the grains are similarly drawn out. The change in the external shape of a grain is made up of a multitude of minute slips, each so small that the grain retains an apparently smooth outline. In Fig. 9 is shown a section through the piece of iron shown in Figs. 6 and 7, after compressing it cold until

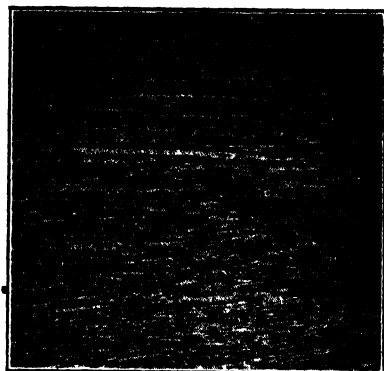


FIG. 10.—Tungsten wire reduced 98.8 per cent in area by swaging. $\times 200$.

its height was reduced about 60 per cent. A much greater degree of deformation is represented in Fig. 10, a section through a piece of tungsten wire. The specimen shown in Fig. 9 was repolished and etched after being compressed, a procedure which effaces slip bands. However, lines are visible within the grains which are undoubtedly due to the cold deformation. Rosenhain considers these to be the traces of slip planes on the plane of the micro-section. Howe is less certain of their nature, and calls them *x-bands*.

Grain deformations are substantially permanent when effected below a temperature known as the "annealing temperature" or "recrystallization temperature." If the metal is subsequently heated above that temperature, the grains recrystallize into new grains, which have a tendency toward equiaxial shape and bear little relation to the old grains. If the deformation is carried out above the annealing temperature, the mechanism is substantially the same, except that the metal anneals during the working. Mechanical work carried out on a metal above the annealing temperature is called "hot working," while, if the temperature is below the annealing temperature, it is called "cold working." Cold work results in a distorted structure and

increased hardness. Hot working produces a normal structure without much change in hardness. Cold working followed by annealing has similar effects to hot working.

When a ductile or malleable crystal (or grain) is loaded sufficiently to cause failure along some crystallographic plane, the fragments formed cohere, and deformation takes place without rupture. The atoms of one fragment are not sufficiently removed from those of the others to lose cohesion permanently. When a brittle crystal is broken, fracture takes place, usually along the crystallographic cleavage planes, and the fragments formed do not stick together. A crystal that is brittle at one temperature may be ductile at a higher temperature. Crystals that are brittle under ordinary conditions of loading may be capable of undergoing plastic deformation under increased hydrostatic pressure. Bismuth and antimony, for example, which are ordinarily quite brittle, can be extruded into wires when sufficient pressure is applied in such a way that the metal is confined on all sides. Increase of pressure brings the atoms into closer contact, facilitating the reestablishment of cohesion bonds along the planes of failure. Increase of temperature serves the same purpose by increasing the amplitude of atomic vibrations.

Brittle metals, such as chromium and manganese, break without permanent deformation, and their cleavage planes are clearly revealed. The fracture then looks crystalline. Ductile metals break only after the grains are greatly drawn out and slip has taken place on very many planes. The fracture then has a more or less fibrous appearance, which does not suggest the inherent crystalline nature of the metal. The same piece of metal, however, when subjected to repeated applications of stress, breaks along the crystallographic planes with practically no permanent deformation, and the fracture may appear crystalline. It is often said that the fatigue has caused the metal to "crystallize," whereas, in reality, the peculiar manner of failure has merely revealed the crystalline structure already present.

Twinned Crystals.—Sometimes grains grow together in such a manner that they are symmetrical structurally with respect to a plane between them. These are called "twin crystals." Usually, the twinning is of such a nature that, if either part of the twin were revolved a certain amount about an axis perpendicular to the twinning plane, the two parts would possess the same orientation and would merge. Sometimes several parallel

twinning planes occur, so that each alternate crystalline strip has the same orientation. This is called "polysynthetic twinning." Figure 11 shows this type of twinning in Alpha brass, a solid solution possessing the essential structural characteristics of pure metal. Figure 12 shows slip bands in Alpha brass twins. It will be noted that these slip bands are continuous through each grain, but change direction at each twinning plane.

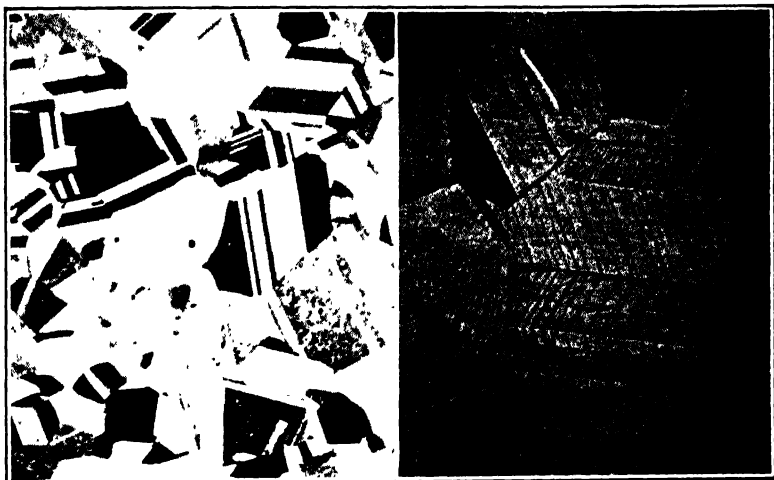


FIG. 11.—Twins in Alpha brass. $\times 50$. (Bassett.)

FIG. 12.—Slip bands in Alpha brass twins. $\times 85$. (Mathewson.)

These twins in brass were produced on annealing after cold working. Twins produced in this way are generally called *annealing twins*, to distinguish them from mechanical twins, which are formed in some metals, notably Alpha iron and zinc, by cold deformation alone. Mechanical twins, in fact, are removed by annealing. Mechanical twins appearing in iron as narrow dark bands are known as *Neumann bands* or *Neumann lines*. They are parallel to certain crystallographic planes.

X-ray Analysis of Opaque Crystals.—This study of the structure of metals is limited by the wave length of the light used. With the highest powered microscopes available, it is possible to distinguish separate particles whose diameters are not less than about $\frac{1}{100,000}$ in. It is theoretically possible, approximately, to double this resolving power by using ultraviolet light of short wave length, but this has not so far been accomplished in a practical manner. At the best, visibility or photography is

limited to distances on the order of 1,000 atom diameters.

Since 1912, methods of crystal analysis by means of x -rays have been developed by Laue, Bragg and Bragg,¹ Hull,² and others, which extend the field of investigation down to the atom itself. X -rays are entirely similar to visible light but have wave lengths of the same order of magnitude as the distances between atoms in crystals. It has been possible, by their use, to determine not only the arrangements of the atoms in metals but the exact distances between them.

The fundamental principle of these methods is similar to that of the ordinary diffraction grating, which consists of a piece of glass or metal on which are ruled a great many parallel and equidistant lines. A beam of monochromatic light falling upon such a grating is diffracted through an angle depending on the wave length of the light and the spacing of the lines on the grating. When white light falls upon the grating, the rays of different wave lengths (or color) are diffracted through different angles, thus forming a spectrum. The grating can be used for the analysis of light and for the exact measurement of the wave length of any particular portion of the spectrum. Or, conversely, monochromatic light of known wave length may be used to determine the spacing of the lines on an unknown grating.

The wave lengths of x -rays are about one ten-thousandth as large as those of visible light, and it would be entirely impossible to construct a grating of appropriate spacings by the usual method of ruling lines. It occurred to Laue that the ordered arrangements of the atoms or molecules in crystals might be used for the investigation of x -rays, since the spacings of the planes of atoms (or molecules) are of the right order of magnitude. This idea has been successfully developed experimentally. The first problem was to verify the supposition that x -rays were, indeed, of undulatory character like ordinary light, and to measure their wave lengths. The process could then be reversed, using monochromatic x -rays of known wave length to measure the spacing of the planes of atoms in a crystal.

The problem differs from that of the ordinary grating, in that the crystal grating extends over three dimensions. The principle

¹ BRAGG, W. H. and BRAGG, W. L., " X -Rays and Crystal Structure," G. Bell and Sons.

² A New Method of X -Ray Crystal Analysis, *Phys. Rev.*, vol. 10. No. 6, Dec., 1917.

can be explained by reference to Fig. 13. The lines p, p, p , etc. represent planes of atoms in a crystal, separated by a common distance, d . A, A_1, A_2, A_3 , etc. are a train of advancing waves of x -rays of wave length λ . Consider that these rays are partly reflected from each plane according to the usual law that the angle of incidence is equal to the angle of reflection. Only a small part is reflected at each plane, the remainder penetrating deeper into the crystal.

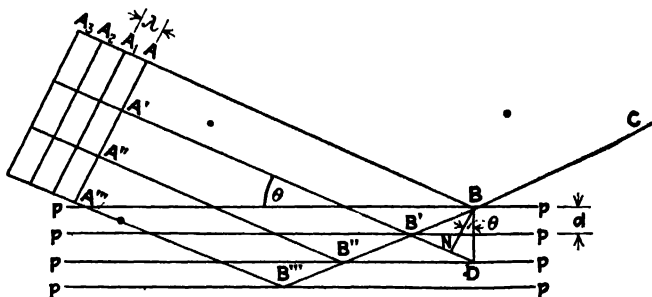


Fig. 13.—Reflection of x -rays by atoms. (Bragg.)

Consider any path of reflection as BC , which is parallel to all other paths of reflection and typical of them. The waves $AB, A'B', A''B''$, etc. join in reflection along BC . These waves are in phase with one another at $AA'A''A'''$, a line perpendicular to the direction of propagation. If they remain in phase with one another after reflection along BC , reinforcement will take place and a strong beam will result. If they are not in phase, the rays will be lost by interference. The necessary condition for reinforcement is that the difference in the paths of these waves must be an integral multiple of the wave length. This condition may be expressed mathematically:

Draw BN perpendicular to AB . Draw BD perpendicular to pp . Prolong $A'B'$ to D . Then:

$$\begin{aligned} A'B'C - ABC &= (A'D + BC) - (A'N + BC) \\ &= A'D - A'N = DN \\ DN &= 2d \sin \theta. \end{aligned}$$

Therefore

$$n\lambda = 2d \sin \theta, \quad (1)$$

where n is any whole number.

This is the fundamental equation. It expresses the fact that, in order for strong reflection to occur, the glancing angle θ must have one of certain definite values. These values are given by:

$$\begin{aligned}\lambda &= 2d \sin \theta_1 \\ 2\lambda &= 2d \sin \theta_2 \\ 3\lambda &= 2d \sin \theta_3, \text{ etc.}\end{aligned}$$

The reflection at the angle θ_1 is called the reflection of the first order, that at the angle θ_2 , reflection of the second order and so on. The possible number of reflections is limited for given values of d and λ , since $\sin \theta$ cannot have a value greater than 1.

Then in the limit:

$$\begin{aligned}n\lambda &= 2d \\ n &= \frac{2d}{\lambda}\end{aligned}\tag{2}$$

For example, if the spacing, atom to atom, equals 5×10^{-8} cm., and the wave length in use is 3.5×10^{-8} cm., $n = \frac{2 \times 5 \times 10^{-8}}{3.5 \times 10^{-8}} = 2.85$. Reflections of the first and second order only are possible.

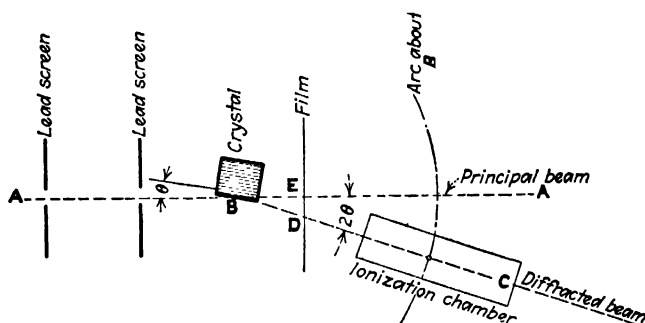


FIG. 14.—Diagram of apparatus for crystal analysis.

An experimental set-up may be represented by the line drawing of Fig. 14.

AA is a pencil of monochromatic x -rays. B is a crystal having crystallographic planes (planes of atoms), as indicated by the fine parallel lines. B is mounted on a pedestal capable of rotation about an axis perpendicular to the plane of the paper.

C is a device for detecting x -rays, such as an ionization chamber. (x -rays have the property of ionizing gases, thereby

causing them to conduct electricity. The conductivity of the gas in the chamber C can be measured by means of an electroscope, which gives a measure of the intensity of x -radiation entering C .) C is mounted to swing on the arc indicated about the same axis as B . By rotating B on its axis and C along its arc, several conjugate positions can be found for which strong reflections will enter C , corresponding to the various orders of reflection. The angles θ_1 , θ_2 , etc. can readily be measured and, given the wave length of the radiation, the spacing of the planes of atoms can be calculated in accordance with equation (1).

By choosing different faces of the crystal, this process can be repeated so as to give the spacings of the various sets of parallel planes, from which data the arrangement of the points in the space lattice can be deduced.

Powder Method of Crystal Analysis.—Suppose that the crystal B in Fig. 14 is properly oriented for a reflection of the first order. If a photographic film, DE , is interposed perpendicular to the beam AB , the diffracted beam will strike it at the point D , on the path of BC . The principal beam, AB , will, for the most part, not be diffracted, and will strike the film at E . Now suppose the crystal to be so mounted that it can be rotated about AA as an axis; during the rotation the correct glancing angle θ_1 will be preserved, and the diffracted beam, BDC , will draw on the film a circle about E as a center. One complete rotation of the crystal will cause it to assume successively *all* of the positions from which it is capable of sending out a reflection of the first order from the particular set of planes in question. The diffracted beam generates a cone of x -rays about AA as an axis. A film interposed cuts out a circle, which is thus the locus of all the possible first-order reflections from this set of planes.

For reflections of higher orders, other circles will be drawn on the film, having diameters increasing with the order of the reflection. It will, of course, be necessary to reset the crystal to the proper glancing angle in each case before carrying out the rotation about AA .

Now suppose the crystal to have its orientation so altered that another set of crystallographic planes diffracts beams onto the film. If the above process of setting the crystal to the proper glancing angles and rotating it about AA is repeated, another set of circles representing the various orders of reflection will be obtained. If the spacing of the planes differs from that

of the first set, the circles will have different diameters, corresponding to the different glancing angles involved.

This process might be repeated for every set of crystallographic planes. The result would be a series of concentric circles. Each circle would be proof of the presence of a set of planes having that particular spacing capable of diffracting a beam through the angle represented by the circle.



FIG. 15.—X-Ray diffraction pattern of aluminum photographed on flat plate.
(Hull.)

Instead of carrying out this process by the systematic method of setting the crystal and rotating it about *AA*, the crystal might simply be caused to assume successively all possible orientations. Exactly the same pattern of concentric circles would then be secured. Or, if instead of a single crystal, a very large number of small crystals with random orientations, is chosen as a specimen the same result is obtained again, without rotating the specimen.

This is the foundation of the generalized method of crystal analysis, or the method of powders, as developed independently in America by Hull and in Germany by Debye and Scherrer. A fine-grained metal possesses the same properties as a powder for this purpose, since it is an aggregate of crystalline grains of mixed orientation. Smaller specimens can be used if they are rotated, as this gives the effect of a greater number of crystal orientations. A single photograph of such a specimen gives all of the possible circles and hence the spacings of all possible crystallographic



FIG. 16.—X-Ray diffraction pattern of aluminum photographed on curved film. (Hull.)



FIG. 17.—Diffraction pattern of molybdenum photographed on curved film. (Hull.)

planes. A diffraction pattern of aluminum obtained by this method is shown in Fig. 15. In actual practice, it is customary to photograph only a small portion of the pattern, and to bend the film into the arc of a circle so that the distances between the lines cut from the large circles are proportional to the angles involved. Patterns of this type are shown in Figs. 16 and 17. Figure 16, in fact, may be considered a magnified section of a portion of Fig. 15. It was photographed on a film bent around an arc about B , whereas Fig. 15 was a flat plate; consequently, the ratios of the distances between successive lines do not have a simple arithmetical relation. However, two bright lines are followed by a broad space, a bright line, a narrow space, two close lines, one brighter than the other, etc.

Atomic Arrangement.—In this discussion many important details have necessarily been omitted, in order to simplify the presentation of the essential principles. It is also beyond the scope of this chapter to go into the actual synthesis of crystal structures, from the data obtained by these methods. These

subjects are completely discussed in the references. For the present, the treatment will be confined to the presentation and discussion of some of the results thus far obtained on metals.

The arrangement of atoms in metals has been found to be extremely simple. The most simple arrangement possible is one in which the atoms occupy positions at the corners of a system of

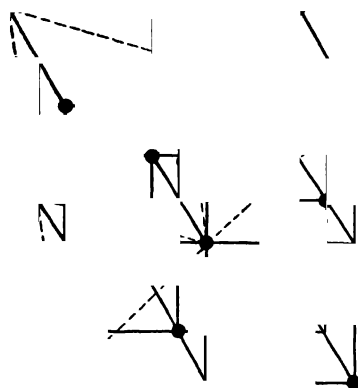


FIG. 18.—Face-centered cubic arrangement of atoms. (Hull.)

equal closely packed cubes. This is known as the "simple cubic arrangement." No metals or other elementary substances have been found to have this arrangement, but it is typical of salts composed of equal numbers of positive and negative ions, such as the alkali halides. The most common arrangement in metals is the face-centered cubic arrangement, shown in Fig. 18, where the atoms are at the corners of a system of equal closely packed cubes and also at

the centers of each cube face. This arrangement may be considered as formed by two simple cubic lattices intersecting each other in such a manner that the corner atoms of one lattice fall at the centers of the faces of the other lattice. All of the atoms in the face-centered arrangement are, in reality, similarly situated. Any particular set of atoms may be equally well regarded as corner atoms or as face atoms. Each atom is surrounded by 12 equidistant and symmetrically situated atoms. This arrangement is one of two which furnish the closest possible packing for a number of equal balls. It is, accordingly, sometimes referred to as the "cubic close-packed arrangement."

The greater the distance between adjacent parallel planes (atomic spacings) the greater is the atomic concentration on the plane and the greater the ease of slip; also, the greater the atomic spacing the less will be the angle of x -ray diffraction. The first line from the main x -ray beam on the x -ray pattern will be produced by the planes of easiest slip and the order of "first-order" diffraction lines gives the order of ease of slip. In the face-centered cubic arrangement, the first four lines are produced by the following planes: 111, 100, 110, and 311, in the order of

their occurrence. There are four sets of 111 planes, three of 100 planes, six of $1\bar{1}0$ planes, and twelve of 311 planes.

The next most common arrangement is built upon a unit cube having an atom at each corner and one at the center. This

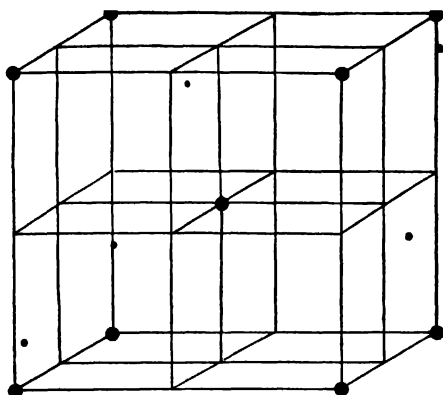


FIG. 19.—Body-centered cubic arrangement of atoms. (Hull.)

is illustrated in Fig. 19. The corner atoms and center atoms are interchangeable, so that, if the system of lines in Fig. 19 had started with one of the center atoms, all the corner atoms

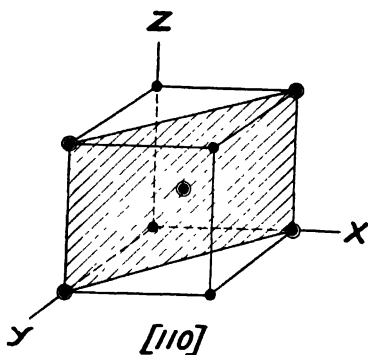


FIG. 20.—One of the 110 planes in body-centered cubic space lattice (cube diagonal).

would become center atoms, and *vice versa*. Each atom is surrounded by eight equally distant and symmetrically situated atoms. This arrangement is not so closely packed as the face-centered arrangement. The three first diffraction lines in the body-centered arrangement are produced by the 110 , 100 , and 112

planes. There are six sets of 110 planes, three of 100 planes, and twelve of 112 planes. Figures 20, 21, and 22 show each of these planes. The black circles represent atoms, and the encircled atoms are on the plane which is cross-hatched.

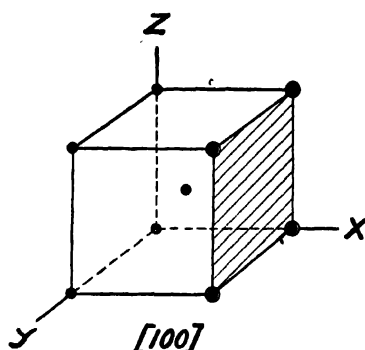


FIG. 21.—One of the 100 planes in body-centered cubic space lattice (cube face).

There is another arrangement commonly found in metals, known as the "hexagonal close-packed arrangement" (Fig. 23).

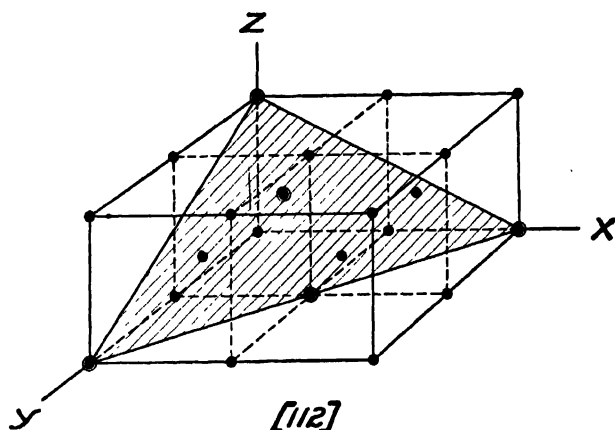


FIG. 22.—One of the 112 planes in body-centered cubic space lattice.

It is equally close packed with the face-centered cubic. The space occupied by a crystal of this sort may be regarded as built up of a series of equal closely packed right-triangular prisms whose bases are equilateral triangles. The altitudes of the prisms are equal to 1.633 times the length of the sides of the

triangles. An atom is located at each prism corner and at alternate prism centers. Each atom is therefore surrounded by 12 other equidistant atoms, as in the face-centered cubic arrangement, but not quite so symmetrically.

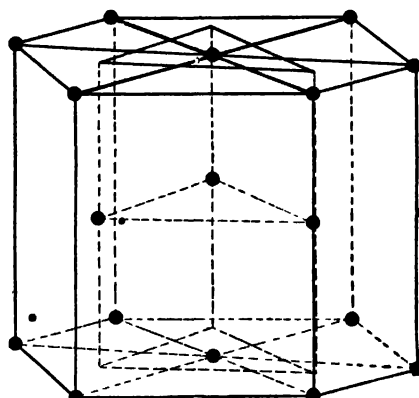


FIG. 23.—Hexagonal close-packed arrangement of atoms. (Hull.)

Allotropy.—Several of the metals are known to exist in two or more allotropic modifications. It has been difficult to define allotropy in a certain manner. The new information on crystal structure suggests that an allotropic change may be defined as a change in atomic arrangement. This definition should furnish a positive criterion of allotropy, hindered only by the experimental difficulties involved in determining atomic arrangements at high temperatures.

Some Results of X-ray Analysis.—Table I (page 5) gives information on the positions of atoms in several metals. The study of the positions of atoms in metals is so recent that only a few generalities can be drawn at present. Some features which may be mentioned are:

1. No metal crystallizing with the face-centered cubic arrangement has been found so far which is not ductile throughout a considerable range of temperature. The face-centered metals are usually ductile even at liquid air temperatures.

2. All of the noble metals so far studied crystallize with the face-centered cubic arrangement.

3. All of the best electrical and heat conductors have face-centered cubic arrangements.

4. Both ductile and brittle metals are found in the body-centered cubic arrangement. This system* seems to be less favorable to ductility than the face-centered, according to Hull.

5. In the hexagonal arrangement, both brittle and ductile metals are found. Hull points out that in the hexagonal arrangement there is only one set of planes parallel to which easy gliding can take place, whereas in the face-centered cubic there are four.

6. Metals having the hexagonal close-packed arrangement harden rapidly under cold deformation.

7. Mechanical twinning (Neumann lines) occurs in metals having the centered cubic and the hexagonal close-packed arrangements. Alpha iron is an example of the former and zinc of the latter. Mechanical twins have also been observed in tin, which is thought to crystallize in the tetragonal system.

8. Annealing twins are certainly most prevalent in metals crystallizing in the face-centered cubic arrangement.

9. Annealing twins have not been observed in metals having the body-centered cubic arrangement, such as Alpha iron, tungsten, and molybdenum.

10. Not all face-centered metals show twinning. Twin crystals have not been observed in aluminum, for example.

Further results of *x*-ray analysis will be considered in subsequent chapters.

CHAPTER IV

THE AMORPHOUS METAL HYPOTHESIS

Although solid metals are, in the main, undoubtedly crystalline in structure, there is reason for supposing that they may exist partly in an amorphous condition, and that those portions which are amorphous may exert a very important influence on the properties of the aggregates. This view was first advanced some twenty years ago by George T. Beilby,¹ largely as a result of his studies on the nature of polished surfaces. It has since been elaborated and extended, notably by Rosenhain,² so that the amorphous metal hypothesis now occupies an important but somewhat uncertain position in modern metallographic theory. It is the purpose of this chapter to recount the principal elements of this hypothesis and to present a critical discussion and a statement of the hypothesis which is believed to be consistent with the results of recent research.

Definition of "Amorphous."—Crystalline materials are characterized by the orderly arrangement of their constituent particles—i.e., atoms or molecules—in definite geometrical patterns. Materials whose molecules do not possess any such regularity of arrangement are amorphous. The term "amorphous" is, thus, in the broadest sense, directly opposed to crystalline. A further distinction must be made. Wood is a material which is decidedly not crystalline, and yet, because of the processes of its growth, it possesses definite directional properties. The arrangement of its atoms or molecules is not entirely haphazard. The same is true of all vegetable and animal tissues. In order to define more specifically what he meant by the term "amorphous" in connection with metals, Beilby used the qualifying adjective "vitreous," narrowing the field to "substances which in some degree resemble the glass-like form assumed by the silicates when they are solidified from the molten state."

¹ BEILBY, G. T., The Hard and Soft States in Metals, *J. Inst. Metals*, No. 2, 1911, pp. 5-43.

² ROSENHAIN and EWEN, Intercrystalline Cohesion in Metals, *J. Inst. Metals*, No. 2, 1912, pp. 149-185.

Amorphous solids are essentially undercooled liquids of great viscosity. The constitution of the liquid is preserved and, with it, the property of fluidity, masked from casual observation by the high viscosity. Glass may be taken as an example. On cooling from the molten state, it passes in a continuous manner from a liquid, which can readily be poured, to the solid commonly known at ordinary temperatures, with a hardness comparable to that of the hardest steel. In spite of this hardness, a rod of glass supported at the ends will sag or "flow" under its own weight in the course of months or years.

It has been pointed out in the last chapter that the regularity of atomic arrangement in crystals leads to mechanical weakness along certain crystallographic planes. The absence of such planes of weakness in amorphous materials leads to great hardness at low temperatures. The hardness and strength of amorphous materials will be discussed later more fully. For the present, it is merely necessary to say that the amorphous modification in most metals is regarded as being harder and stronger than the crystalline at ordinary temperatures.

Amorphous Films on Rubbed Surfaces.—The studies of Beilby referred to above showed that the operation of polishing causes a surface flow of the material being polished. The action of abrasive materials is essentially one of cutting. The grinding of a metal surface by an abrasive, such as emery, consists in the cutting of minute grooves, the emery particles acting as cutting tools. When such a surface is polished or burnished, the surface layers of the metal are caused to flow, bridging or filling up the grooves left by the emery. Working with the mineral calcite (calcium carbonate), which is especially suitable for such observations, Beilby found that the flowed surface possessed certain properties which distinguished it from the unpolished crystal face. It was harder, as tested by the loaded needle, and its hardness was the same in all directions, whereas the hardness of the natural crystal face varied according to the direction in which it was measured.

Perhaps the most significant thing is the way in which the polishing operation gradually smooths over the scratches, finally obliterating them and leaving a surface with an appearance "absolutely homogeneous and vitreous, like a coating of varnish or enamel." Furthermore, that this smooth surface is merely a coating is demonstrated by the fact that the scratches are again

revealed when the surface layer is dissolved in hydrochloric acid. Beilby concluded that the flowed material is rendered amorphous by the action of polishing. This amorphous film was assumed to be in a condition of great mobility at the instant of formation, so that, under the influence of surface tension, it would assume a very smooth surface. It was then supposed to solidify or "set" in the final hard, glassy state.

It had already been shown that the permanent deformation of metals takes place by a kind of block movement on certain crystallographic planes, known as "gliding planes" or "slip planes." Beilby postulated that the rubbing of the crystal fragments over each other on the slip planes generates films of amorphous metal comparable to the surface films produced by polishing. Like the surface films, they were supposed to pass through a mobile stage and then become hard and rigid. Now the ductile metals are greatly hardened and at the same time made brittle by deformation carried out below the annealing temperature, whether such deformation be effected by cold drawing, rolling, pressing, or other means. According to Beilby's theory, this "hardening results from the formation at all the internal surfaces of slip or shear of mobile layers similar to those produced on the outer surface by polishing. These layers retain their mobility for only a very brief period, and then solidify in a vitreous amorphous state, thus forming a cementing material at all surfaces of slip or shear throughout the mass." The increased hardness is thus attributed to the presence of a framework or matrix of a modification of the metal possessing greater specific hardness than the crystalline modification.

After this stiffening of the metal, further deformation is forced to take place on new slip planes, thereby producing more amorphous metal and still greater hardness. There is a practical limit to the amount of cold deformation that a metal will endure. Further attempts cause rupture. Thus in wire drawing, if the process is carried too far, the wire draws hollow or splinters. Even before this stage is reached, maximum hardness and strength are produced. Overdrawing reduces the strength. This is regarded by Beilby as due to the exhaustion of available crystalline material. The crystalline modification of the metal is regarded as the sole source of plasticity, and when the available supply is exhausted the metal becomes incapable of further deformation.

Recrystallization.—Metals which have been hardened by cold work are softened by heating to a suitable temperature. The softening is accompanied by the restoration of ductility and by the substitution of a clearly crystalline structure of equiaxed grains for the disordered structure found after cold working. This operation is called *annealing*, and is a regular part of most industrial processes involving the cold deformation of metals. The softening is explained by Beilby's theory as due to the recrystallization of the amorphous metal produced by the cold work. Disappearance of the amorphous metal would, of course, involve the simultaneous disappearance of the hardness and brittleness supposed to be due to it.

Crystallization of an amorphous solid or undercooled liquid is a common occurrence. Glass and vitreous silica crystallize or "devitrify" when exposed for a long time to temperatures at which they are somewhat soft. The presence of crystalline nuclei greatly facilitates this transformation. Beilby considers the recrystallization of metals to be strictly analogous to that of other amorphous materials in the presence of nuclei. The nuclei are the fragments supplied by the breaking up of the original crystalline grains. The amorphous metal is regarded from the physico-chemical viewpoint as identical with the liquid phase. Hence, it must be unstable at all temperatures below the melting point of the metal and is prevented from reverting to the stable crystalline form only by its rigidity due to the low temperature. On raising the temperature of a metal, the atomic mobility becomes sufficient for the unstable amorphous phase to crystallize about the nuclei already present.

Other Methods of Producing Amorphous Metal.—Beilby did not consider deformation to be the only means for the production of amorphous metal. He recognized that it is not possible to retain metals in the amorphous condition by rapid cooling from the molten state, as is the case with glass, vitreous silica, and many other typical amorphous solids. He did, however, advance the suggestion that "the evolution of a dissolved gas when a critical point is reached may so effectually prevent or modify crystallization that the metal is hardened." And again,

Sometimes a very minute addition of a second substance to a pure metal is sufficient to prevent crystallization in the regular way, or even to prevent it altogether. The product is then more rigid and less plastic than the pure metal.

This statement was offered as an explanation of the fact that solid solutions of two metals are usually harder than the pure metals, the case of gold and silver being mentioned as an example. Another suggestion was that amorphization might be brought about by flow occurring in a cooling mass as a result of shrinkage strains. Certain samples of electrodeposited copper are found to be very hard and to possess a structure somewhat resembling that of cold-worked metal. Annealing causes recrystallization and softening. From these observations Beilby concluded that "the deposition of the metal under conditions of strain had caused the molecular aggregation to be of the amorphous type." These suggestions are interesting to note in tracing the development of the theory. Beilby sums up thus:

The development of the maximum intrinsic hardness of the metals can thus be brought about in many different ways, but in every case it appears to depend on the special development of the cohesive force which is associated with the amorphous or non-crystalline aggregation of the molecules.

What Cements Crystalline Grains Together?—In 1912, Beilby's hypothesis received a very important extension, consisting in the proposition that the amorphous phase exists not merely in cold-worked metals but is also a normal constituent of all metals in the form of an intergranular cement.¹ Beilby's original hypothesis that amorphous metal is formed on slip planes during plastic deformation was put forth to explain hardening. The postulation of an amorphous intergranular cement was advanced to explain an entirely different set of phenomena, which will now be briefly described.

When pure metals that are in what may be called a normally healthy condition are broken, the path of fracture is found to pass almost exclusively through the grains, rather than between them. The grain boundaries appear to be stronger than the grains themselves, rather than weaker, as might be expected. When metals are broken at temperatures just under their melting points, however, the conditions are reversed, fracture following the grain boundaries.

¹ The conception of an amorphous cement between the grains of metals was published practically at the same time by Bengough (*J. Inst. Metals*, No. 1, 1912, pp. 123-190) and by Rosenhain in a discussion of Bengough's paper.

Permanent deformation of metals consists of plastic deformation of the crystalline grains, by the process of slip or gliding. If the grains possess any inherent plasticity, as is normally the case in the ductile metals, then fracture through the grains is necessarily preceded by some plastic deformation of the grains and a general deformation of the metal as a whole. Transcrystalline fracture is, therefore, accompanied by a ductile break. Intergranular fracture at high temperatures, on the contrary, takes place in a brittle manner—*i.e.*, with little if any general deformation of the metal. The cohesion between grains has become so small that they pull apart before sufficient load can be transmitted to deform them.

The assumption that the grains of metals are held together by a cement of a vitreous amorphous nature explains these phenomena in a very satisfactory manner. At the lower temperatures this cement is hard and strong, so that the necessary loads can be transmitted to the grains to deform them and finally cause rupture to pass through them. As the temperature is raised, the amorphous cement gradually softens,¹ so that at high temperatures it is very weak. The grains then readily pull apart without any appreciable deformation.

Time Factor in Loading Amorphous Material.—Since the atoms (or molecules) of amorphous materials do not occupy fixed positions with respect to one another, such materials can be deformed by the gradual shifting of the relative positions of their particles. The atoms in a crystal of metal are held in substantially fixed positions in the crystal lattice. Deformation therefore takes place by the simultaneous movement of a large number of atoms. A correspondingly large number of atomic cohesion "bonds" must be broken at one time. The result is that the strength (or what is the same thing, its elastic limit in shear) of a crystal is definite. The cohesion bonds in an amorphous material may be broken very gradually—almost one atom at a time. The force required to produce deformation is, therefore,

¹ It was Bengough's view that the amorphous cement disappeared entirely at high temperatures and that the intergranular fractures were due to the absence of any cementing material. Rosenhain's view that the lessening of the cohesion between the grains is due to the softening rather than the disappearance of the amorphous metal was considered preferable by Bengough and is now generally accepted by the adherents of the amorphous metal theory.

very small. Such small forces must, of course, act for considerable periods of time in order to effect appreciable deformations.

There is a distinct and important time effect in the rupture of metals at high temperatures. At any given temperature which lies well above the annealing temperature of the metal, but not too close to the melting point, either intergranular or transcrystalline fracture can be produced at will by varying the rate of applying the load. This is illustrated by some tests carried out on copper wire at a temperature of 950° C.¹

Time required to break	Tensile strength	Type of fracture
1 min.	710 lb. per square inch	Intergranular, brittle
5 sec.	2,500 lb. per square inch	Transcrystalline, ductile

It will be noted that not only is the type of fracture changed by increasing the rate of loading, but the strength is very greatly increased. This is explained on the assumption of an amorphous intercrystalline cement by the known properties of solid amorphous materials. Attention has already been called to the fact that glass will flow under its own weight acting for a long period of time, whereas it is perfectly elastic up to a stress of perhaps 30,000 lb. per square inch under loads acting for short periods. The typical combination of fluidity and hardness possessed by amorphous solids is perhaps illustrated even better in the properties of pitch. At ordinary temperatures, pitch can be pulverized by means of hammer blows. If the particles of powder thus produced are put in a receptacle, the force of gravity alone is sufficient to weld them into a single coherent mass of pitch. This welding may require considerable time, but it is so effective that even the air bubbles are slowly forced to the surface. Pitch can be deformed into any shape desired if sufficient time is taken. A barrel of pitch, for example, can be emptied by allowing it to flow very slowly from a small hole. At any time during this process of flow, a sharp hammer blow will shatter into fragments the stream of flowing pitch. Pitch is thus either hard and brittle or soft and plastic, according to the rate of deformation

¹ JEFFRIES, ZAY, Effect of Temperature, Deformation, and Grain Size on the Mechanical Properties of Metals, *Trans. Am. Inst. Mining Eng.*, vol. 60, pp. 474-562.

attempted. Resistance to rapid deformation is very great, but deformation can be effected slowly by extremely slight forces.

Now the crystalline grains of a metal are supposed to be held together by an amorphous metal cement whose properties at high temperatures resemble those of pitch at ordinary temperatures. At the freezing point of the metal the liquid or amorphous metal has practically no resistance to deformation. At the same time the crystalline metal has very considerable resistance to deformation. The case is similar to that of water and ice at the freezing point of water. As the metal cools, the undercooled liquid or amorphous metal at the grain boundaries increases in viscosity, so that at very low temperatures it has great hardness. At the same time the hardness and strength of the crystalline metal increase, but at a less rapid rate. At "high temperatures," which in the case of metals means at temperatures above that of recrystallization, the amorphous metal is softer than the crystalline.

Suppose a piece of metal, such as the copper wire mentioned above, be subjected to a small tensile load which is insufficient at the temperature of the test to deform the crystalline grains (the force required to deform a crystal is practically independent of any time effect). If this small load is allowed to remain on the test specimen, it will in time cause flow in the viscous amorphous cement and the grains will finally be pulled apart, without having themselves undergone any deformation. The fracture will then be of the intergranular, brittle type.

Suppose a similar specimen to be loaded rapidly to a much higher stress. The amorphous cement will sustain high stresses for short periods of time, so that, if the load is applied rapidly enough, a stress can be reached which is high enough to deform the crystalline phase. Fracture will then take place through the grains instead of between them, and will be accompanied by considerable general deformation of the piece as a whole.

Hypothesis of Amorphous Metal Cement.—This is, in brief, the amorphous metal cement hypothesis as proposed by Rosenhain and Ewen. It was advanced primarily to account for the cohesion between the grains of a metallic aggregate and the changes in cohesion with change in temperature. The development of the hypothesis leads, of course, to conclusions regarding other phenomena, particularly hardness. The amorphous metal at the grain boundaries was supposed to be the same as that

proposed by Beilby as the cause of the hardness produced by cold deformation. Any increase in grain boundary surface must, therefore, result in an increase in hardness. This afforded a ready explanation of the fact that the hardness of metals increases as the grain size becomes smaller. Carrying the idea to the extreme, Rosenhain proposed that the great hardness of hardened steel is due to "the presence of an extremely minute network of amorphous layers" surrounding the very fine grains of Alpha iron which result from the rapid transformation of Gamma iron. He regarded the amorphous iron as being especially hard in this case because of iron carbide in solution.

Beilby's theory of hardening by the formation of amorphous metal and Rosenhain's conception of an amorphous intercrystalline cement comprise what may be called the fundamental ideas of the amorphous metal hypothesis. These ideas have in some form gained a rather wide acceptance in England and America, although they have not been so favorably received on the Continent. There is at present no unified opinion regarding the details of the hypothesis, which is quite to be expected, considering its newness and its speculative nature. It must be recognized that this hypothesis concerns some of the most important properties of metals, and therefore deserves very careful inquiry and consideration both as to the fundamental ideas and their detailed development.

Can Metal Be Produced Entirely Amorphous?—The first question to be considered should, perhaps, be that of the reality of amorphous metal. It is possible by means of the x-ray spectrometer literally to "look into" a metal and recognize the presence of crystalline material. Unfortunately, however, there is no such positive test for the presence of amorphous material. The most direct proof of the reality of amorphous metal would, of course, be the production of metal *entirely* in the amorphous condition. Beilby attempted to do this by mechanical deformation, and he selected wire drawing as a suitable process because of its drastic nature. After having drawn wires of silver, copper, and gold to as much as 14 times their original lengths, he concluded that they still contained crystalline metal and that it is impossible by mechanical deformation to convert a metal entirely into the amorphous modification. In addition to the microscopic observations upon which his conclusion was largely based, there is an abundance of confirming evidence of a more positive nature.

Beilby considered that he had produced a totally amorphous mass of metal by compressing very fine gold powder precipitated from aqueous solution. He described his product as harder and, less plastic than other forms of gold, and also resistant to recrystallization at 350°C. , or about 100°C. above the temperature required for the recrystallization of cold-drawn gold wires, a property he attributed to the absence of crystalline nuclei. It is now known that chemically precipitated metallic powders, even when composed of the finest particles, are perfectly crystalline, so that masses formed by compressing them are themselves predominantly crystalline.

It is quite certain that no totally amorphous mass of solid metal has been produced. A little consideration of the molecular structure of amorphous bodies is interesting in this connection. The materials which are most readily obtained in amorphous form, such as pitch, glass and vitreous silica, always have several atoms to the molecule. Some of the chemical elements, of which sulphur is an example, can also be obtained in an amorphous condition. A sulphur molecule contains 8 atoms. Metals are monatomic in all conditions of aggregation, and therefore crystallize more freely. A single atom can obviously find its place in a crystal lattice more easily than can a molecule containing several atoms. It will therefore be very difficult to obtain metals in an entirely amorphous solid state.

Possible Structures at Grain Boundaries.—The best evidence for the existence of amorphous metal is probably to be found in the conditions at grain boundaries. In the original statement of their intercrystalline cement hypothesis, Rosenhain and Ewen advanced the idea that the crystallization of metals takes place by the addition of crystal units containing large numbers of atoms. In the region where two crystals abut against one another—that is, at the grain boundaries—there would have to be some metal which could not attach itself to either crystal because of being too small in amount to form crystal units. Furthermore, since the crystalline grains have different orientations, the units or blocks of one would not fit in with the blocks of the other, and interstices of irregular shape would be left which could not be filled up with other crystals no matter what their orientation. The metal remaining in these interstices must then retain the structure of the liquid—*i.e.*, must be amorphous.

The diagram in Fig. 24 shows this condition in a schematic way, the shaded areas representing the interstices filled with amorphous metal.

This conception is no longer tenable, inasmuch as it now appears quite certain that the "crystal units" consist of one atom each. The actual conditions must nevertheless be very

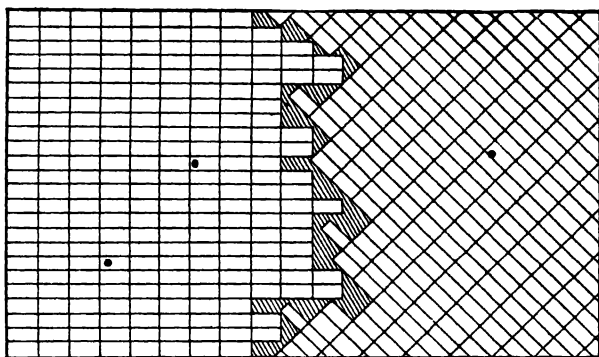


FIG. 24.—Schematic representation of condition at grain boundary. (Rosenhain and Ewen.)

similar, in a qualitative way and on a smaller scale, to those represented in the diagram. Certainly, where two crystals of different orientation meet, it is not geometrically possible for all of the atoms present to have places in an undisturbed space lattice without leaving some voids.

There are three possible conditions: (1) There are voids between the two crystals; (2) there is a zone in which some of the atoms are held in *both* crystal lattices, in which case the lattices would be distorted at the surface of contact; or (3) there is a zone of disorganized or *amorphous* metal.

There is no way known at present of determining the actual structure at the grain boundaries of metals. It is certain that, under various conditions of temperature and rate of loading, metals behave as they would if their grains were held together by a cement of a substantially amorphous nature. There are many other properties of metals which are consistent with the assumption of an amorphous cement, and none, to the authors' knowledge, which are inconsistent. The hypothesis is thus plausible from the structural viewpoint and logical, in that it offers satisfactory explanations of the properties of the grain boundaries

of metals. This is enough to justify the utilization of the idea as a working hypothesis—but one can go even further. The amorphous metal cement hypothesis is at the present time the *only* satisfactory explanation of the effect of temperature and rate of loading on the strength and manner of rupture of metals. This fact confers upon it an added degree of probability.

Impurities at Boundaries.—The only alternative theory that has been advanced is based upon the assumption that, even in what are ordinarily termed “pure” metals, there are appreciable quantities of impurities forming eutectics melting below the melting point of the metal. When the metal is heated to high temperatures, these eutectics melt and form molten layers around the grains of solid metal. The molten layers have very little strength, and hence allow the grains to be pulled apart on the application of small loads. There are a great many objections to this explanation. The phenomena to be explained occur with great distinctness in metals of the very highest purity. Any eutectic that might be present in such a pure metal would necessarily have a very high melting point, little short of that of the theoretically pure metal. In any case, the melting point of the eutectic would be *fixed*. This is not the case with the temperature separating intergranular from transcrystalline fracture, which varies with the rate of loading or duration of load. Furthermore, intergranular fracture can be produced at any temperature from the recrystallization temperature to the melting point. The intergranular eutectic hypothesis is untenable from this point of view. An additional objection is that it does not sufficiently explain the time effect, especially on the tensile strength, such as quoted on page 69 for copper.

In the authors' opinion it is justifiable to conclude that the metal at the grain boundaries is or simulates an amorphous material. It is not possible to reach any definite conclusions regarding the degree of disorganization of this material or the thickness of the films around the grains. Although definite information on these points is desirable, it is not necessary to the formulation of a useful theory. The essential fact is that the grain boundary metal possesses mechanical properties like those of a vitreous amorphous substance.

The amorphous cement occupies a very important place in the structure of metals, inasmuch as it is continuous. Nevertheless, the amount of crystalline metal is so preponderant that, as a rule,

metals never exhibit properties like those of an entirely amorphous material. In the tests of metals at high temperatures which have been referred to, the tensile strength varies with the rate of loading in the same manner as that of an amorphous material. That is, the longer the time taken in breaking the specimen the smaller the load required. The elongation, on the contrary, follows an exactly opposite course. Metals broken by small loads acting for long periods of time show little if any elongation, while an amorphous material, like pitch or glass (at a red heat), shows more elongation the slower the loading.

Zinc-aluminum-copper Alloy of Peculiar Properties.—An alloy¹ has recently been described which is of special interest, for the reason that both its strength and its ductility are affected by the rate of loading in the same manner as are those of amorphous materials. The alloy is the ternary eutectic of zinc (89 per cent), aluminum (7 per cent), and copper (4 per cent). The principal metal, zinc, recrystallizes at room temperature, so that the "high-temperature" phenomena of less fusible metals, like iron, are in this case obtained at ordinary temperatures. The properties are shown best by the alloy after it has been subjected to considerable rolling at about 250° C. A strip of the metal in this condition can be bent double between the fingers, if the bending is carried out slowly, taking, say, 5 min. An attempt to bend the strip quickly causes it to break with a sharp snap. This is exactly the behavior that would be expected of an amorphous material like pitch. This simple experiment demonstrates in a qualitative way the effect of rate of loading on the properties of this alloy. A quantitative expression of the same effects is found in the curves reproduced in Fig. 25.

This alloy resembles amorphous materials in another respect—namely, the return flow or "creep" after deformation. If a strip of amorphous material, like pitch, is bent in a given direction and then released, it springs back somewhat in the opposite direction, but does not immediately assume a stable position. It continues to creep back slowly at a steadily diminishing rate. All metals, with the exception of single crystals, behave in a similar manner, but the creep is usually so slight that rather sensitive instruments are required to detect it. Rosenhain's alloy exhibits this property to a degree comparable with pitch. The curves in

¹ ROSENHAIN, HAUGHTON, and BINGHAM, Zinc Alloys with Aluminum and Copper, *J. Inst. Metals*, No. 1, 1920, pp. 261-317.

Fig. 26 show the return creep for three materials, plotted to the same scale, except that for glass the deformations are magnified $14\frac{1}{3}$ times.

The exceptional degree to which this alloy resembles materials that are entirely amorphous is attributed by the present authors

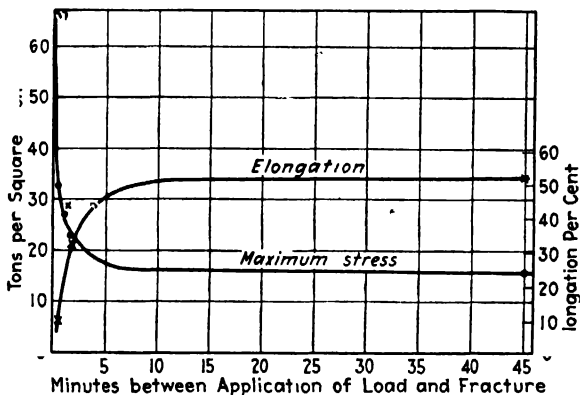


FIG. 25.—Effect of rate of loading on properties of Zn-Al-Cu alloy. (Rosenhain, Haughton, and Bingham.)

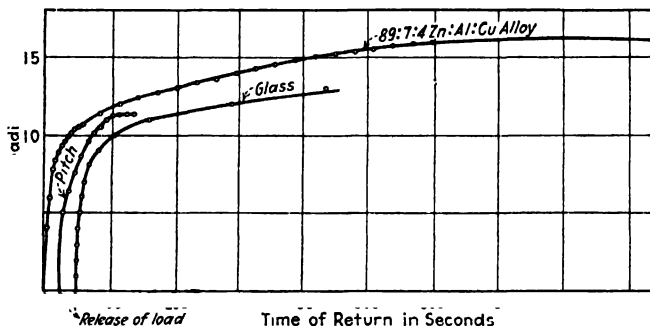


FIG. 26.—Return flow in glass, pitch, and zinc alloy. (Rosenhain, Haughton, and Bingham.)

to a very fine grain size stable at temperatures normally in the recrystallization range. The alloy consists of the three structural constituents of the ternary eutectic. These crystalline constituents are divided very finely by the rolling process. Grains of a pure metal broken up in this way by deformation carried out above the recrystallizing temperature promptly unite so that the metal is left in a moderately coarse-grained condition. In this case, however, the eutectic constituents cannot unite and, by

interfering with grain growth in the matrix (zinc), cause the final grain size to be very small. This, coupled with the probable high specific hardness of the crystalline constituents, accentuates the effect of the properties of the grain boundary metal. The discovery of the properties of this alloy is important, because this is the only case on record in which the properties of the amorphous "phase" completely mask those of the crystalline constituents in a metallic aggregate.

Other Properties of Grain Boundaries.—There are many phenomena for which the amorphous metal cement hypothesis furnishes a convenient explanation, but for the explanation of which the assumption of an amorphous cement is not necessary. They are, therefore, not to be regarded as strong evidence for the existence of an amorphous metal cement, but merely as facts which are consistent with the hypothesis. One group of such facts may be comprised in the statement that the grain boundaries of metals are particularly subject to chemical attack and to the penetration of gases. A bronze can be disintegrated into its individual crystals by the action of mercury (Desch),¹ which dissolves away the grain boundary metal. Dickenson has shown that certain failures of manganese bronze were caused by the penetration of solder between the grains while the metal was under tensile stress. The solder must, of course, be molten to have this effect. It is usually necessary in this, as in other cases of a similar nature, for the metal to be under tension in order for any rapid intergranular penetration to take place.

Cold-worked articles of brass, such as cartridge cases, are subject to a type of failure known as "season cracking." After standing for some time, perhaps years, the article develops cracks which are shown by microscopic examination to be intergranular. It has been stated by Rosenhain that failure analogous to season cracking may take place in certain rolled aluminum-zinc alloys in the entire absence of corrosive agencies. There is no doubt, however, that corrosion, either by the atmosphere or by other agencies, greatly hastens the process. Brass articles are often tested for susceptibility to season cracking by immersion for a short time in a solution of mercurous nitrate. Metallic mercury is liberated and penetrates the grain boundaries of the brass where tensile stress exists. Cracking then follows quickly.

¹ DESCH, The Solidification of Metals from the Liquid State, *J. Inst. Metals*, No. 2, 1919, pp. 240-263; *Chem. Met. Eng.*, vol. 21, p. 773, Dec. 24, 1910.

In the carburizing of steel, the carbon penetrates more rapidly by way of the grain boundaries than through the crystals themselves. Diffusion follows the grain boundaries, as can also be seen by reheating a graphitized iron to temperatures above the critical and then cooling rapidly.¹ The carbon will be found to have been reabsorbed into the iron by way of the grain boundaries.

Commercially pure copper is embrittled to a ruinous extent by annealing in a reducing atmosphere, such as hydrogen. The hydrogen is supposed to penetrate the metal and reduce the copper oxide which is always present. The steam formed is unable to escape and its disruptive force is the cause of the bad effect on the copper. In this case again the penetration of the hydrogen takes place partly by way of the grain boundaries.

Many other examples could be cited to illustrate this susceptibility of the grain boundaries to attack. It is to be assumed that the amorphous cement supposed to exist at the grain boundaries is electropositive to the crystalline metal, since it more closely resembles the liquid in structure, and therefore has a higher internal energy content. This would account for its greater susceptibility to chemical attack and penetration by molten metals. The penetration by gases would be ascribed to the freedom of motion of the atoms in the amorphous metal, which would not present a rigid barrier to the penetration of gas molecules, as would the fixed atoms in the crystal lattice. These facts can also be explained on the assumption that the structure at the grain boundaries of metals consists of two perfect crystal lattices interlocking with the formation of voids free from any amorphous metal.

Vacuum Etching.—Another phenomenon closely allied to these is one known broadly as “vacuum etching.” Rosenhain and Ewen sought to demonstrate the existence of amorphous metal at the grain boundaries by determining the relative losses in weight of coarse- and fine-grained metals when heated in vacuo. They showed that the losses of the fine-grained specimens were much greater than those of the coarse-grained specimens, and attributed this to the presence of greater quantities of amorphous metal, which is quite logically supposed to have a higher vapor pressure than the crystalline metal. These observations are, however,

¹ ARCHER, R. S., Graphitization of White Cast Iron, *Am. Inst. Mining Engr.*, Feb. Meeting, 1920.

explained with equal satisfaction on the basis of any of the three possible grain boundary structures mentioned above.

Special attention has been called by one of the authors¹ to the flow of metals at high temperatures. In making filaments for certain classes of electric lamps, it is desirable to have tungsten wire which will not sag under its own weight when heated to high temperatures. It has been found that at high temperatures fine-grained wires sag much more than do coarse-grained wires. This is consistent with the theory that the sagging consists in flow in the layers of amorphous cement around the grains. Small grains would lead to greater flow because of more grain boundary surface. An alternative explanation is that the sagging of the wires consists in a migration of the grain boundaries—that is, grain growth—under the influence of stress and temperature. Such grain growth would take place in a direction tending to relieve the stress, which would cause the wires to sag. The greater sagging of the fine-grained wires would be due to the greater boundary surface and to the greater tendency of small grains to grow. It is probable that this is a factor in the observed flow (although not the only one), but such a mechanism does not account for the strength properties of the grain boundaries. The authors therefore prefer to consider that the grain boundaries are amorphous, because this accounts for all of the observed properties.

Amount of Amorphous Metal Produced by Cold Work.—

The question of the formation of amorphous metal during plastic deformation is perhaps more difficult than that of its existence at grain boundaries. There is, again, no direct evidence and there are in this case no phenomena which cannot be explained without assuming the formation of amorphous metal on all of the slip planes. Beilby advanced his hypothesis primarily as an explanation of hardening. It is the opinion of the present authors that hardening can be satisfactorily accounted for on the basis of a rearrangement of crystalline material, as described in subsequent chapters. Any amorphous metal formed would, of course, contribute to the hardening, but it is not necessary to assume its presence for this purpose.

Beilby's hypothesis was, as indicated above, based largely on his studies of polished surfaces. Having concluded to his

¹ JEFFRIES, ZAY, *The Amorphous Metal Hypothesis and Equi-cohesive Temperatures*, *Trans. Am. Inst. Metals*, 1917, p. 300.

satisfaction that the surface layers of polished metals are in an amorphous condition, he assumed that the internal friction on slip planes during deformation also generates layers of amorphous metal. There is some doubt that the surface layers of polished metals are entirely or even largely amorphous, but even granting that they are entirely amorphous, this cannot be considered as more than a suggestion that similar layers are formed on the internal surfaces of slip. The processes—polishing and slip—differ in two important respects. The friction in polishing is between the metal and a dissimilar surface, usually a cloth charged with fine particles of metallic oxide. Secondly, the amount of relative motion between the two surfaces in the case of polishing is enormously greater than in the case of crystalline displacement by slip.

Beilby's Original Hypothesis Impossible.—A rough calculation will suffice to show that Beilby's hypothesis as originally proposed is untenable. According to this hypothesis, amorphous metal is developed at *each* slip plane and slip occurs only *once* on each plane. From many observations of slip band, made mostly on fairly coarse-grained specimens, it appears that the maximum extent of motion along a slip plane during a single deformation ranges from 1,000 to 5,000 atom diameters—seldom greater. It also appears that the extent of slip is less the smaller the grain size. Normally, therefore, the average extent of a single slip is probably well under 1,000 atom diameters. Assume, for example, a single crystal in the shape of a 1-in. cube, of a metal having 100,000,000 atoms per linear inch. Assume that slip generates amorphous layers 2 atoms in thickness, which is about the minimum that could be considered amorphous. The number of possible slip planes on the cross-section would then be 50,000,000. A slip on each of these planes to an extent of 1,000 atom diameters would result in a general extension of 500 in., after which all of the metal would be amorphous.

But copper can be extended by cold swaging and drawing, without intermediate annealing, to as much as 5,000 times its original length and the metal is still preponderantly crystalline! Tungsten wire drawn to 200,000 times its original length without intermediate annealing still gives strong x-ray patterns, showing that it is predominantly crystalline! Beilby's scheme of plastic deformation is not consistent with such facts.

The wires of copper, silver, and gold with which Beilby experimented were in no case drawn to more than 14 times their original lengths, and he stated that the maximum strength was reached after drawing to from 3 to 5 times the original length. This increased strength and hardness he attributed to the formation of layers of amorphous metal, yet the proportion of metal converted to the amorphous condition would not have to be so very large. The greatest possible proportion actually so converted in his wires may be judged by the fact that wires drawn 1,000 times as much are still predominantly crystalline. It is believed, therefore, that any amount of amorphous metal that may be produced by drawing a wire to 5 times its original length cannot, in itself, be responsible for the increased hardness and strength.

The abundance of crystalline material left in a cold-drawn wire is further shown by the fact that wires drawn until they have lost practically all of their ductility when tested at ordinary temperatures regain their ductility to a large extent on cooling to the temperature of liquid air. Ductility is at low temperatures dependent on the presence of a very considerable amount of crystalline metal, since amorphous metal is considered to become increasingly hard and brittle as the temperature is lowered.

The evidence shows that whatever amorphous metal may be formed during cold deformation is very much less in amount than indicated by Beilby. It follows that the importance attached to the specific hardness of amorphous metal as the cause of hardening has also been greatly exaggerated.

What Causes a Slip to Halt?—The conclusion that there are not formed on *all* of the surfaces of slip vitreous amorphous layers which prevent further slip on those surfaces does not preclude the possibility that some amorphous metal is produced during plastic deformation. A little consideration will show us that the block movements on slip planes, or "slips," may be divided into two rather distinct classes.

When a single crystal of metal is broken in tension, it might be expected that the final failure would take place on the first plane on which slip occurs. Such, however, is not the case, since large single crystals of ductile metals are themselves ductile and draw out under tension into the form of wedges. This shows that failure does not occur on the first slip plane. The conclusion must be that something happens during the process of slip which causes the resistance to further slip on that plane to

be *greater* than the resistance to the starting of slip on some new plane. The slip may be said to be "self-stopping."

In ordinary pieces of metal, which are aggregates of many small grains, it is probable that only a small proportion of the slips are self-stopping. The majority of the slips are brought to rest by end resistance. There is every indication that the resistance to further movement on the surfaces of such slips is *less* than the resistance to the starting of slip on a new plane. At the beginning, therefore, a slip plane is a surface of weakness.

All this amounts merely to saying that a certain amount of movement or of *time*, or both, is required for the building up of resistance on a slip plane. The "weakened and building-up" stage corresponds to the "mobile" state of Beilby. It may be that amorphous metal is actually in process of formation in this stage. The later stage, when the slip has become self-stopping, undoubtedly represents an altered structural condition at the surface of slip, which must necessarily involve some local disorganization of the crystalline metal. This disorganization may or may not be sufficient in kind and depth to justify the assumption of *vitreous* amorphous layers. The indications are that the disturbance does not penetrate very deeply and also that the differences in orientation between two adjacent crystal fragments are never very great. *Certainly, the surface condition at slip planes, even in the self-stopping stage, does not prevent further movement on the same surface.* In the first stages of slip there is no reason to assume the presence of any amorphous metal, and in the later stages it is not justifiable to assume the presence of vitreous layers so rigid as to prevent further slip.

At the grain boundaries the conditions are different. The shapes of the original grains must change in a manner depending on the change in shape of the piece of metal taken as a whole. No matter what the direction of extension, the grain boundary surface is increased by cold work. Each slip intersecting a grain boundary produces one "lapped-over" fragment, the surface atoms of which may be utilized to increase amorphous metal at the grain boundary. As deformation becomes severe, the grain boundary layer of amorphous metal should become thicker by the same process. It is the authors' opinion that the chief generation of amorphous metal by cold plastic deformation occurs here.

Summary.—1. Certain properties of cast metals, or metals which have been worked and annealed, are satisfactorily explained only on the assumption that the metal at the grain boundaries is in a substantially amorphous condition.

2. There is not at present sufficient evidence to determine whether this grain boundary metal possesses the perfectly amorphous structure indicated by the term “vitreous.” There is, however, enough evidence to justify the assumption that the grain boundary metal possesses the essential deformational and strength characteristics of typical vitreous amorphous materials.

3. The hypothesis that crystalline grains of metal are cemented with amorphous metal—*i.e.*, the amorphous metal cement hypothesis—is not inconsistent with any of the known properties of metals.

4. Plastic deformation at temperatures below the temperature of recrystallization generates additional amorphous metal at the boundaries of the original grains.

5. There is no means of estimating with any exactness the quantities of amorphous metal which may be present under various conditions. There is certainly more amorphous metal in severely cold-worked metals than in annealed metals. Even the most severely cold-worked metals are predominantly crystalline. The amorphous metal hypothesis is a qualitative rather than a quantitative conception, so that it is perhaps not necessary to form very definite ideas as to the possible *quantities* of amorphous metal.

6. The formation of vitreous amorphous metal at all the internal surfaces of slip in the manner postulated by Beilby is not tenable, and the hardness produced by cold working can be readily explained without the assumption of such amorphization.

7. There is developed on some of the surfaces of slip a condition of cohesion greater than that in the undeformed crystal. This condition may presumably be due to a locally disorganized structure, but the assumption of a layer of *vitreous* amorphous metal is not necessary, nor is it consistent with all of the facts.

8. Whereas the amorphous metal theory of deformation postulates that when slip has once occurred on a particular plane no further slip on that plane is possible, the evidence available indicates not only that further slips on a “used” plane are possible but that they *must* occur in the course of the maximum deformation that can be effected.

9. The conception of an intergranular, amorphous metal cement furnishes a very good explanation of certain deformational and strength properties of metals and a very useful working hypothesis. The importance attached to the specific hardness of amorphous metal as a cause of hardening has been greatly exaggerated.

CHAPTER V

GRAIN GROWTH AND RECRYSTALLIZATION

The crystalline structure of metals was discussed in Chap. III. This chapter will deal more specifically with the sizes and shapes of grains produced on the solidification of metals, on grain growth in the solid state, and on recrystallization.

When a metal freezes, the sizes and shapes of the crystalline units or grains vary in accordance with the conditions obtaining at the time of crystallization. In general, there is no distinction made between crystallization and solidification, since the latter is due to the former. As a rule, rapid solidification produces smaller grains than slow solidification. The grain size of cast metals, provided they have not been plastically deformed, cannot be changed by heating below the melting point. This is true no matter what the grain size in the cast metal.¹ When a cast metal is plastically deformed at a temperature high enough so that no "strain hardening" results, microscopic examination shows that new and usually smaller grains have been produced. Working a metal at such temperatures is termed "hot working." Plastic deformation has thus caused the grains to undergo some change which usually produces several grains from each of the original ones. Supposing the metal under consideration is copper, and assuming that the temperature of working is 600° C., severe working will produce a marked "refining" of the structure—that is, the grains will have increased greatly in number and will have decreased proportionately in size. If the metal is now heated to, say, 800° C., it will be observed that grain growth has taken place and that there are fewer and larger grains. The melting point of copper is 1,083° C.; this grain growth occurs, therefore, while the metal is in the solid state. In what is termed "normal grain growth," the higher the temperature and the longer the time at heat the larger will be the grain size. In some cases grain

¹ Iron is an exception to this general rule, in that it undergoes an allotropic change at 900° C., accompanied by a complete change in crystal structure with the formation of new grains. Grain growth also takes place in some cast alloys as a result of phase changes.

growth is very rapid at a given temperature for a short time, after which longer exposure seems to produce no further change. This is a condition of metastable equilibrium. An increase of temperature usually produces further grain growth in these cases.

Definition of Recrystallization.—When a metal is plastically deformed at a temperature so low that “strain hardening” results, it is said to be “cold worked.” Microscopic examination shows that the grains have been deformed in about the same manner and magnitude as was the piece of metal taken as a whole. Except in the soft metals, like lead, tin, and zinc, these distorted grains do not change at room temperature. On heating, however, a temperature is reached, different for different metals and for various degrees of cold work, at which the distorted grain structure is replaced by new grains, usually approximating an equiaxed shape. By *equiaxed grain* is meant one whose diameter is approximately the same in all directions. Hardness tests show that most of the “strain-hardening” effect is lost with this change in structure. This change is usually referred to as “recrystallization,” and the lowest temperature at which new grains visible under the microscope appear may be called the *recrystallization temperature*. Recrystallization temperatures for certain metals, after severe cold plastic deformation, are given in Table IV.

TABLE IV.—RECRYSTALLIZATION TEMPERATURES

Metal	Approximate lowest recrystallization temperature, de- grees Centigrade	Metal	Approximate lowest recrystallization temperature, degrees Centigrade
Iron	450	Magnesium. . .	150
Nickel . . .	600	Tantalum . . .	1,000
Gold	200	Tungsten. . . .	1,200
Silver. . . .	200	Molybdenum . .	900
Copper . . .	200	Zinc	Room temperature
Aluminum . .	150	Lead	Below room temperature
Platinum . . .	450	Tin	Below room temperature
		Cadmium	About room temperature

It is intended to present here a definite conception of the mechanism of recrystallization which will define recrystallization

in a fundamental manner. The values given in the table must be considered as approximations, and are selected with reference to the lowest temperatures after severe cold work, which will produce new grains *visible under a high-powered microscope*. The recrystallization temperature is lower the greater the amount of cold work, the lower the temperature of working, the purer the metal, the smaller the grains before deformation, and the longer the time of exposure at temperature. It is only a matter of usage that the temperature of the beginning of recrystallization should be selected with reference to the appearance of grains which can

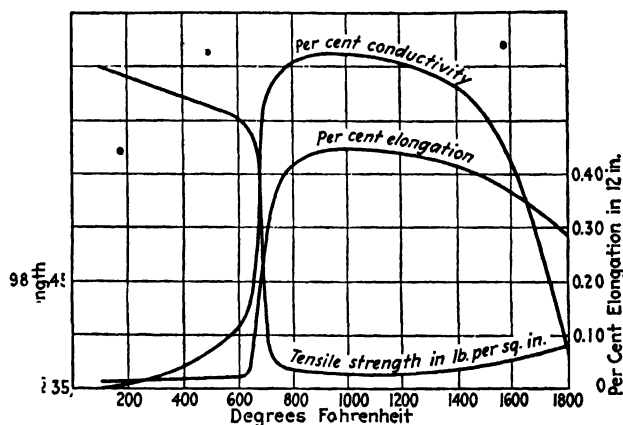


FIG. 27.—Effect of annealing on the room temperature properties of cold-drawn copper wire. (Bardwell.)

be seen with a microscope; other measurements, such as tensile strength, electric conductivity, or hardness, give more sensitive indications of the first changes of structure. It is true, however, that when new grains can be seen, the change toward the properties of the annealed metal is marked. Technically, *recrystallization* is the structural change produced in a cold-worked metal on changing from the strain-hardened state to the annealed state. Although there are an infinite number of stages, curves relating certain physical properties to temperatures of heating a cold-worked metal will often show sharp changes within a small temperature range and a gradual change both above and below this range. Such curves are given in Fig. 27, showing the tensile strength, elongation, and electrical conductivity changes in cold-worked copper heated at various temperatures. A sharp break in all of the curves corresponds to a structural change, the elon-

gated (strain-hardened) grains having been replaced by small equiaxed grains. The sharpness of the changes in Fig. 27 shows the justification for a term such as "recrystallization" to designate the temperature range within which they occur.

If a strain-hardened metal is heated to a temperature just below that of recrystallization, no visible grain growth takes place. On heating to any higher temperature, grain growth takes place, the higher temperatures and extended exposures producing the larger grains.

When metal powders are briquetted and heated to temperatures somewhat below their melting points, grain growth takes place. In the case of tungsten, molybdenum, or nickel powder, the density of the briquet may be only 60 per cent of that of the "solid" metal but, after heating to a high temperature but below the melting point, the density becomes about the same as in the cast or worked metals. On heating these briquets, the grain size normally¹ increases both with the temperature and with time of exposure.

Electrodeposited metals are crystalline. The grain size may be large or small but heating such a metal may cause grain growth below the melting point.

Iron is unique in its grain growth characteristics because of the allotropic change in a temperature region permitting grain growth. If iron is cast, it forms grains of Gamma iron above 900° C., crystallizing with a face-centered cubic lattice. On cooling, Gamma iron changes completely into a body-centered lattice at about 900° C., and this transformation gives rise to entirely new grains. If the iron is kept below 900° C., it behaves much like any other metal within a similar temperature range. It can be cold worked and hot worked and the grain growth characteristics can be studied at temperatures up to 900° C. On heating above about 900° C., however, the structure again changes completely into new grains of Gamma iron. Every time iron is caused to change from one crystal lattice to the other a new set of grains is produced. Pure Gamma iron cannot be cold worked, because at the lowest temperatures at which it is stable it cannot be strain hardened.

Average Grain Size.—Before proceeding with a more detailed account of grain growth phenomena, it will be well to explain what is meant by some of the terms used.

¹ Deviations from this rule will be considered later.

Grains are three-dimensional bodies roughly polyhedral in shape. Observation of them especially for the purpose of determining grain size, is usually on a polished plane section. The quantity actually measured is, therefore, not the volume of the grain, but some linear dimension or area. Furthermore, the grains in a given piece of metal of even the most uniform structure always vary rather widely in size. Rosenhain has pointed out that, for practical purposes, it is perhaps the size of the largest grains which is of most importance, and some specifications have been written upon this basis, rejecting material which contains grains exceeding a certain stated diameter or area. It is, of course, probable that the observed plane section of any particular grain does not represent its *maximum* cross-sectional area, but it is also probable that the maximum grain area observed on a polished section containing a large number of grains *does* represent closely the maximum size of the grains.

It is more common to measure the *average* grain size over the observed area. The various methods of doing this will not be discussed, but a preferred method (which has been described fully by one of the authors¹) will be outlined for purposes of illustration. The specimen is photographed at a known magnification, or, if a photograph is not desired, the image on the ground glass of the camera may be used. A circle is drawn on the ground glass or on the micrograph representing a certain area on the surface of the specimen, selected so as to include a fairly large number of grains, preferably over 50. A count is then made of the number of grains totally enclosed and also of the number intersected by the circumference of the circle. Twinned portions of grains are not counted as separate grains. The sum of the number totally enclosed plus half the number intersected gives the equivalent number of whole grains within the area of the circle from which the average number of grains per unit area or the average area per grain may be readily calculated. It should be emphasized again that this quantity does not represent the maximum cross-sectional area of the average grain, but the average cross-sectional area such as would be cut by a plane taken at random.

A value, which will be called the average grain diameter, is obtained by taking the square root of the average grain area. This diameter has no exact physical meaning. It represents what

¹ JEFFRIES, Grain Size Measurements in Metals, *Met. Chem. Eng.*, vol. 18, p. 185, 1918.

would be the length of side of the grains if they were all square. Actually, the average grain diameter, determined in this manner, is sufficiently close, for all practical purposes, to the average intercept cut by a straight line through a large number of grains.¹

When it is desired to make computations on the basis of volume, the hypothetical square grain may be extended to a cubical grain. The average grain volume is then equal to the cube of the average grain diameter.

It will be seen from the above that grain size measurements are only approximate. Some have objected to this inaccuracy and attempted by mathematical analysis to arrive at more exact expressions. The objection and attempt are unjustified in view of the real significance of the figures. The properties of metals are not affected to any marked extent by a variation in grain size of 25 or even 100 per cent. Indeed, such variations commonly occur from point to point in a supposedly uniform metal. The methods in common use for measuring and expressing grain size are, therefore, amply exact for the purpose.

Grain growth may occur without affecting the grain size as expressed by average grain area or diameter. During the first stages of growth the total number of grains within a given area does not change, and hence the average grain size remains constant. It is not until some of the grains are completely absorbed that the measured grain size indicates the change. Some other means must be used for detecting *slight* grain growth. For most practical purposes, however, the grain growth considered is of such magnitude that it is well shown by changes in the measured average grain size.

Elongated Grains.—When the grains depart widely and consistently from an equiaxial shape, as in cold-worked metal, it is often better to determine grain size by the intercept method—that is, by counting the grains intersected by a given length of straight line. It will be understood that the grains of a cold-worked metal are broken up into fragments which are in many respects equivalent to individual grains, but that the reference here is to the counting of the original grains. The average grain

¹ It is perhaps most scientific to express grain size in terms of the number of grains per unit area, since this is the quantity directly measured. The authors prefer, however, for general purposes, to express grain size in terms of the average grain diameter in inches, with the object of giving as concrete a conception as possible of the actual magnitudes involved.

diameter may be determined in this way both in the direction of working and at right angles to this direction. A complete description of the grains requires measurements in three directions, corresponding to coordinate axes, and made on two surfaces usually at right angles to each other. The ratios of the average grain diameters thus determined indicate the shape of the grains and the amount of deformation that the metal has undergone.



FIG. 28.—Unstrained grains simulating cold-worked metal in drawn tungsten wire. $\times 250$. (Sykes.)

The term *worked metal* will be used to denote metal which has been subjected to mechanical working of any kind, hot or cold, by rolling, forging, pressing, swaging, drawing, or otherwise.

The word *strain* is used very commonly in connection with grain growth, in a sense not altogether obvious. From the physical or mathematical viewpoint, any deformation is a strain, including the elastic deformation represented by the first portion of a "stress-strain" diagram. But an elastic deformation does not constitute a strain, according to usage in connection with grain growth. Strain is sometimes used to denote stress, and at least carries an implication of this meaning. "Strain" as used in these pages does not necessarily involve stress. A *strained metal* or grain may be defined as one which has been permanently deformed in such manner as to harden it. A hot-worked metal is not strained. The strain of a cold-worked metal is removed by annealing.

The hardness produced by work is called *strain-hardness* or *work-hardness*.

Unstrained grains are normally equiaxed in shape, but exceptions are very common. When a metal containing material which mechanically obstructs grain growth is subjected to considerable working, either hot or cold, it is sometimes found to exhibit grains which are consistently elongated in the direction of the working, even after thorough annealing. An example of this type of structure in tungsten is shown in Fig. 28. These grains are unstrained, though not equiaxed. A distorted grain shape suggestive of cold working is not, therefore, to be regarded as proof of strain.

When a metal solidifies in a chill mold, it is often found that long grains grow out at right angles to the walls of the mold. These grains are referred to as *columnar* and they are, of course, unstrained. If the mold is circular, or nearly so, in cross-section, the grains converge toward the center, and may then be referred to as *radial grains*.

Dendritic Grains.—The appearance of the grains of a cast metal on a plane surface cut through the metal usually gives no indication of the mechanism of their formation. Each grain

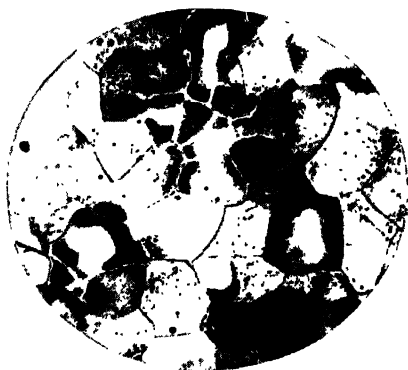


FIG. 29.—Cast 90:10 brass. $\times 50$. (Bassett.)

appears uniform within its own boundaries and does not suggest that it has grown by a process of dendrite formation. That such is the case is revealed by examining an exterior surface of the metal which has been allowed to solidify freely and upon which the dendrites will usually be found in relief. An illustration was given in Chap.

III. Figure 29 is a micrograph of a cast brass containing 90 per cent copper and 10 per cent zinc. The structure approximates that of a pure metal, showing polyhedral grains uniform in appearance within themselves except for slight changes in etching tint due to concentration of the zinc near the grain boundaries. This effect is known as *coring* and regularly occurs during the solidification of alloys which in equilibrium consist of homogeneous solid solutions.

Cored Crystals.—As the amount of impurity increases, the coring effect becomes more marked. In Fig. 30 is shown a cast brass containing 70 per cent copper and 30 per cent zinc. Under equilibrium conditions about 36 per cent of zinc is soluble in copper in the solid state, but equilibrium is not attained during solidification and the structure shows marked coring with perhaps the separation of a second phase. The dendritic structure of the primary copper-rich grains is clearly shown. Figure 31 shows a similar structure in cast monel metal, which contains about 67 per cent nickel, 28 per cent copper, and 5 per cent iron and manganese. Both this alloy and the 70:30 brass, after working and annealing, exhibit perfect solid solution structures, indistinguishable under the microscope from those of a pure metal. These illustrations show not only the tendency of metals to crystallize in the form of dendrites but also that the solid solution alloys are not homogeneous solid solutions in the cast state. This is important because the discussions below deal with grain growth in substantially pure metals and solid solution alloys, which, after a homogeneous structure is produced, follow the same laws of grain growth as pure metals.



FIG. 30.—Cast 70:30 brass. $\times 50$.
(Bassett.)



FIG. 31.—Cast monel metal. $\times 75$.
(Merica.)

On solidification, the amount of the added element in an alloy of the solid solution type influences the grain size. This is particu-

larly true in case of sharp variations of temperature between different parts of the solidifying alloy. Whereas pure metals cast in iron molds, or otherwise caused to solidify rapidly, nearly always show smaller grains than when cast in sand molds, solid solution type alloys often show larger grains when cast in chill molds. There seems to be a certain temperature gradient and composition favoring the formation of large grains. The solidification of an ordinary steel ingot in an iron ingot mold seems to produce the proper conditions for large grains in the exterior of the ingot and considerably smaller grains in the interior. It should be remembered that the grain size of cast metals is always large as compared with that ordinarily found in worked metals.



FIG. 32.—Coarse-grained tungsten briquet fused at center. $\times 25$.

Nucleus Action.—The effect of existing crystals on the crystallization of a liquid is well known. If a crystal of a salt is put in a saturated water solution of the salt and the temperature lowered, the existing crystal grows larger. The added material assumes the same orientation as the original crystal. If the temperature is lowered very gradually, no new crystals may form. This is only one of many cases illustrating that when a liquid solidifies existing crystals form *nuclei* on which the liquid crystallizes. A

good example of this rule was observed when a coarse-grained tungsten ingot was heated by the passage of electric current until the central or axial portion fused. Figure 32 shows that the grains in the resolidified portion are continuations of the grains in the unfused portions.

When a fine-grained tungsten ingot was fused in the center, however, the metal resolidified in such manner that each grain in the resolidified portion was adjacent to about 100 of the original grains. The structure of such an ingot is shown in Fig. 33. This

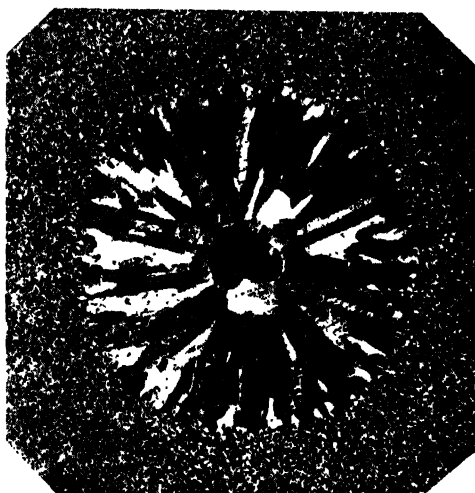


FIG. 33.—Fine-grained tungsten briquet fused at center. $\times 6$. (Sykes.)

relatively coarse-grained structure is produced in spite of a rapidity of solidification perhaps seldom equaled in any other metal. The fusion of the ingot breaks the electrical contact and in about one minute the ingot cools from 3,400 to about 50° C. Such a cast structure does not show grain growth in the solid state, even with long exposures at temperatures slightly below the melting point.

Normal Grain Growth in Solid Metals.—Grain growth in the solid state in worked metals and solid solution alloys can be illustrated by the behavior of Alpha brass. The structure of a 70:30 brass as cast is shown in Fig. 30. After hot working or cold working and heating to a temperature around 600° C., the structure is that of a homogeneous solid solution composed of equiaxed grains. In worked brass the grains are nearly always



FIG. 34.—68:32 brass, cold rolled, 50.9 per cent reduction in thickness. $\times 75$. (*Bassett and Davis.*)



FIG. 35.—68:32 brass, reduced cold 50.9 per cent and then heated at 300° C. $\times 75$. (*Bassett and Davis.*)



FIG. 36.—68:32 brass reduced cold 50.9 per cent and then heated at 350° C. $\times 75$. (*Bassett and Davis.*)

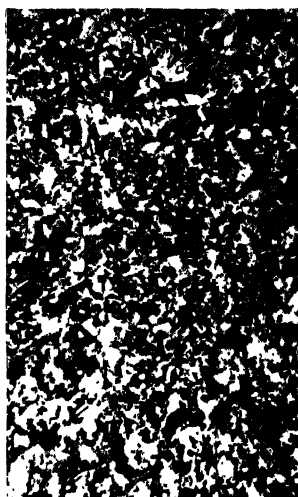


FIG. 37.—68:32 brass reduced cold 50.9 per cent and then heated at 450° C. $\times 75$. (*Bassett and Davis.*)

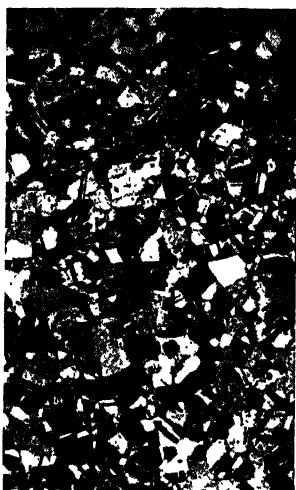


FIG. 38.—68:32 brass reduced cold 50.9 per cent and then heated at 550° C. $\times 75$. (*Bassett and Davis.*)



FIG. 39.—68:32 brass reduced cold 50.9 per cent and then heated at 650° C. $\times 75$. (*Bassett and Davis.*)



FIG. 40.—68:32 brass reduced cold 50.9 per cent and then heated at 750° C. $\times 75$. (*Bassett and Davis.*)



FIG. 41.—68:32 brass reduced cold 50.9 per cent and then heated at 850° C. $\times 75$. (*Bassett and Davis.*)

twinned, although twins are not found in the casting. The history of change in grain size with change in temperature in a 68:32 brass after 50.9 per cent reduction in thickness by cold rolling is shown in Figs. 34 to 41 inclusive. No grain growth takes place until a temperature of about 275° C. is reached and the cold-worked structure is completely replaced by small equiaxed grains at 400° C. after a 30-min. exposure. As the temperature increases, the grain size increases.

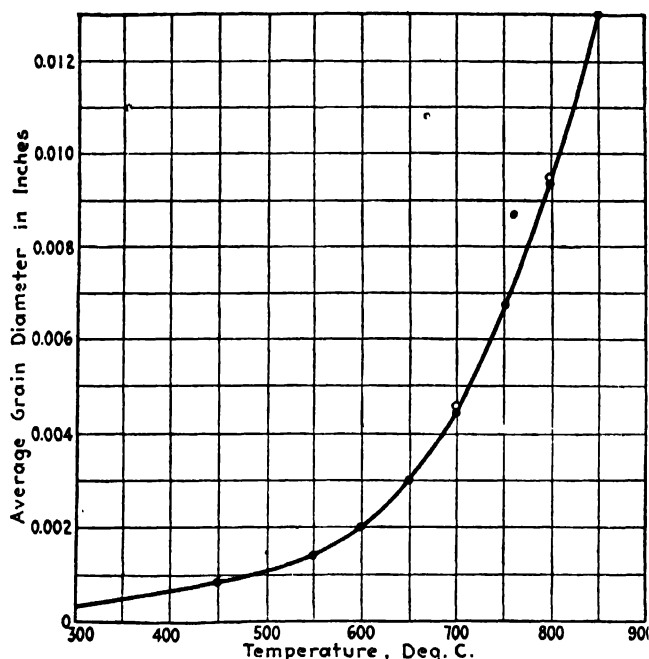


FIG. 42.—Effect of 30-min. annealing on the grain size of 68:32 brass cold rolled 50.9 per cent. (Bassett and Davis.)

The increase in grain size with temperature can be seen qualitatively in the micrographs and is plotted in Fig. 42. The shape of this curve is similar to that found for many metals by various observers, including Mathewson and Phillips¹ working on Alpha brass; Mathewson² on copper-tin alloys with 2.4 and 8 per cent

¹ MATHEWSON and PHILLIPS, Recrystallization of Cold-worked Alpha Brass on Annealing, *Trans. Am. Inst. Mining Eng.*, vol. 54, pp. 608–670, 1916.

² MATHEWSON, Metallographic Description of Bronzes from Machu Picchu, Peru, *Am. J. Sci.*, vol. 40, p. 546, Dec., 1915.

tin; and Mathewson and Thalheimer¹ for copper. Rapid increase in grain size begins at about 700° C. for copper.

Although this type of curve is normal for many metals, there are many factors which may and often do cause marked deviations. McAdam² shows that cold-worked Armco iron, annealed for either 7- or 14-hr. periods, has a fairly constant grain size up to about 800° C., above which temperature there is a marked grain growth. His temperature-grain size curves are more flat at low temperature than the one shown in Fig. 42, but the increase in grain size above 800° C. is more pronounced than in Alpha brass above 600° C. One of the authors has found that the normal grain size-temperature curve for briquetted and sintered tungsten powder³ is more nearly a straight line than that of Fig. 42. Sometimes when abnormal growth occurs, the curve may depart entirely from the normal type within certain temperature ranges.

The time of exposure at the various temperatures is an important factor in the resulting grain size, especially at the lower temperatures. In Alpha brass a grain size is reached after a comparatively short time, say 30 min., at 650° C., which does not change to any marked extent with longer exposures. If the temperature is 325° C., the time necessary to establish apparent equilibrium grain size is measured in days. Figure 43 shows the time necessary at various temperatures to produce a given amount of softening in Alpha brass. If, however, the temperature is raised to a little below the melting point, a fraction of a minute is often sufficient to produce a grain size which does not change noticeably on further exposure. Incandescent lamp filaments of tungsten operated at a temperature of about 2,100° C. usually exhibit growth until "burn out," which is sometimes as long as 90 days' total heating. The same filaments can be heated to a temperature just below the melting point (3,400° C.) and in a few minutes, or sometimes in a fraction of a minute, a grain size will be produced which does not change noticeably when the filament is subjected to a lower temperature.

¹ MATHEWSON and THALHEIMER, Comparisons between Electrolytic Copper and Two Varieties of Arsenical Lake Copper with Respect to Strength and Ductility in Cold-worked and Annealed Test Strips, *Am. Inst. Mining Eng.*, vol. 55, pp. 446-485, 1916.

² McADAM, Grain Size of Iron as Affected by Temperature, *A.S.T.M.*, vol. 18, Part II, *Tech. Papers*, pp. 68-86, 1918.

³ JEFFRIES, The Metallography of Tungsten, *Am. Inst. Mining Eng.*, vol. 60, pp. 588-656, 1919.

A severely cold-drawn nickel-iron alloy containing 56 per cent iron and 44 per cent nickel, with a melting point of about $1,475^{\circ}\text{C}$., was heated to $1,200^{\circ}\text{C}$. for 30 sec. and a grain size was developed which did not change with longer exposure at that or lower temperatures. The same alloy required several hours at 725°C . to produce a similar stability of grain size, although the grains were much smaller than those produced at $1,200^{\circ}\text{C}$.

Armco iron containing only 0.02 per cent carbon was pressed cold and heated to 850°C . At the end of 1 hr. the average grain diameter was 0.0022 in. At the end of 10 hr. this had increased to 0.0077 in. and after 168 hr. the average grain diameter was 0.25 in. How much longer this growth would have gone on is not known, as the test was not continued.

The important conclusions from these observations are: (1) that under some conditions of temperature, particularly at relatively high temperatures, a grain size is established in a very short time, which is stable so long as the metal is not subjected to a higher temperature; and (2) that there is in some metals an intermediate temperature range (which is around $2,100^{\circ}\text{C}$. for tungsten and 850°C . for iron) at which grain growth continues for long periods and very large grains may be developed. This intermediate temperature range is not found in all metals. When it is found, an abnormal grain size may develop. Carpenter and Elam¹ report that large grains are developed in commercial aluminum sheet severely worked and annealed for 2 weeks at 550°C .

Recrystallization.—A great amount of work has been directed toward the study of the phenomena of recrystallization. Recrystallization has been defined above as the change from the strain-hardened to the unstrain-hardened condition. When recrystallization is complete, the small unstrained grains grow into larger unstrained grains in accordance with the general rules just considered.

The greater the degree of strain hardening the lower will be the temperature of recrystallization. Consequently, with a metal of a given composition—*i.e.*, a given degree of purity—anything which will increase the degree of strain hardening will decrease the recrystallization temperature. The amount of deformation effected below the recrystallization temperature is

¹ CARPENTER and ELAM, *Crystal Growth and Recrystallization in Metals*, *J. Inst. Metals*, No. 2, 1920.

one factor influencing the degree of strain-hardening. The general rule is that the recrystallization temperature is lower the greater the amount of cold work.

Mathewson and Phillips show that in Alpha brass, previously annealed at 800° C., recrystallization after 4 per cent reduction in area by cold rolling requires a temperature of 650° C., and after 40 per cent reduction the temperature is 350° C. for a 30-min. anneal. Carpenter and Elam show that commercial aluminum sheet previously annealed for 6 hr. at 550° C., and then elongated 2 per cent at room temperature, did not show recrystallization, or at least complete recrystallization after a heating of 65 hr. at 500° C. With 4 per cent or more elongation, recrystallization was complete under these conditions of time and temperature. With severe cold work the recrystallization temperature may be lowered to 200° C. or less. Usually, in such cases the grain size is smaller the greater the previous deformation.

Grain size prior to cold deformation is an important factor in connection with the degree of strain hardening and hence affects the recrystallization temperature. The smaller the grains the greater is the strain-hardening effect of a given amount of deformation and the lower is the recrystallization temperature. Fine-grained metal elongated 1 per cent may have a lower recrystallization temperature than a coarse-grained metal elongated 5 per cent or more. This disparity in grain size prior to cold deformation may even produce such marked difference that a coarse-grained metal elongated as much as 5 per cent will not recrystallize at a temperature which will cause normal grain growth in an annealed but fine-grained sample of the same metal. For example, a severely cold-worked aluminum sheet heated for several hours at 250° C. will recrystallize. The grains will be small. If the same piece is heated to 300° C., grain growth will take place. A very coarse-grained sample stretched 5 per cent cold may show no signs of recrystallization at 300° C.

Time of exposure at temperature is an important factor in the temperature of recrystallization (refer to Fig. 43.) A cold-worked metal which might show only partial or no visible signs of recrystallization in 5 min. might show complete recrystallization in an hour or more. So far as tests go, it seems that the recrystallization temperature becomes lower the longer the time of exposure. When the temperature which will cause recrystallization with a few hours' exposure is found, a slight decrease in temperature

causes an enormous increase in time to produce recrystallization. So great is this effect that a temperature is found not far below the ordinary recrystallization temperatures which would necessitate an exposure of years to produce recrystallization.

The temperature of deformation is also a factor in determining the recrystallization temperature. The lower the temperature

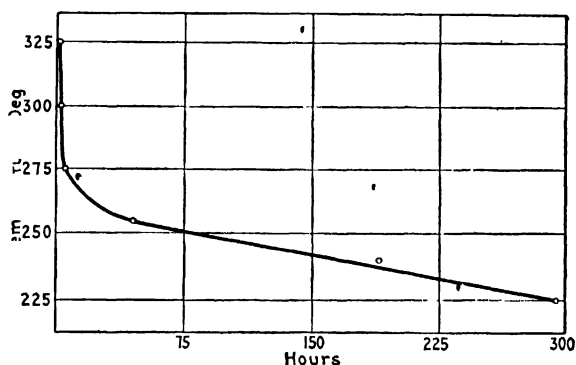


FIG. 43.—Time-temperature relations for 3-point drop in scleroscope hardness of 70:30 brass cold rolled 40 per cent. (Mathewson and Phillips.)

at which the deformation is effected the lower will be the recrystallization temperature. A possible exception to this general rule is iron worked at a temperature near 200° C.

The purity of a metal is also an important factor in connection with the recrystallization temperature. As a rule, a solid solution alloy has a higher recrystallization temperature than the solvent metal. For example, severely strain-hardened Alpha brass containing 34 per cent zinc has a recrystallization temperature of about 300° C., whereas severely strain-hardened copper has a recrystallization temperature of about 200° C. Impurities producing mechanical obstruction to grain growth also increase the recrystallization temperature.

The recrystallization temperature not only varies for different treatments of different pieces of the same metal, but it varies within the same piece of metal if a homogeneous condition does not exist. Since with mild cold deformation and large grains it is impossible to produce a condition even approximating homogeneity, such samples usually recrystallize over a considerable range of temperature. The greater the amount of strain hardening the smaller this range will be—that is, the complete change in structure from strained to unstrained grains will take place



FIG. 44.—Alpha brass cold rolled 4 per cent and then heated 30 min. at 550° C. $\times 75$. (*Mathewson and Phillips.*)



FIG. 45.—Alpha brass cold rolled 8 per cent and then heated 30 min. at 550° C. $\times 75$. (*Mathewson and Phillips.*)



FIG. 46.—Alpha brass cold rolled 12 per cent and then heated 30 min. at 550° C. $\times 75$. (*Mathewson and Phillips.*)



FIG. 47.—Alpha brass cold rolled 15 per cent and then heated 30 min. at 550° C. $\times 75$. (*Mathewson and Phillips.*)

within a small temperature range. Since the properties depend on the structure, there is a marked change with a small temperature change.

If the temperature at which recrystallization is just complete is considered, it is observed that the lower the recrystallization temperature the smaller the grain size. When some condition is varied which raises the temperature of complete recrystalli-

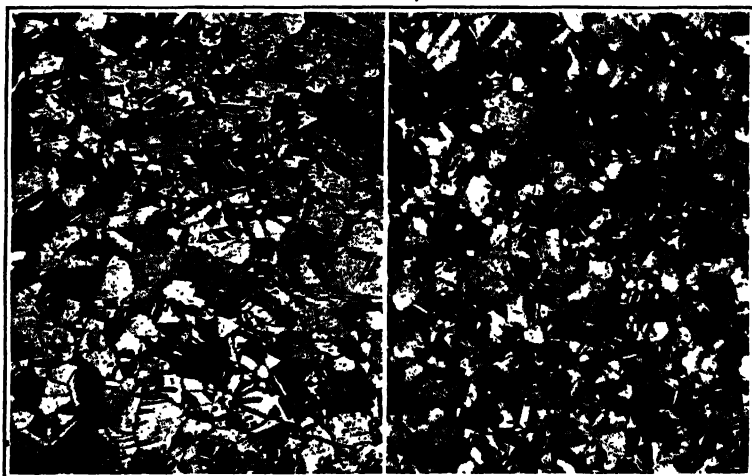


FIG. 48.—Alpha brass cold rolled 23 per cent and then heated 30 min. at 550° C. $\times 75$. (Mathewson and Phillips.)

FIG. 49.—Alpha brass cold rolled 50 per cent and then heated 30 min. at 550° C. $\times 75$. (Mathewson and Phillips.)

zation, such as the amount of deformation, the grain size after complete recrystallization is larger than with the lower recrystallization temperature. With a given recrystallization temperature there is a certain *minimum* grain size which can be produced. This minimum is less the lower the recrystallization temperature in any particular metal.

The disparity in grain size produced by varying the recrystallization temperature tends to disappear as normal grain growth proceeds above the recrystallization temperature. Equality of grain size is produced only at high temperatures. Figures 44 to 49, of Alpha brass, cold worked different amounts and then heated for 30 min. at 550° C., show how the grain size becomes smaller as the recrystallization temperature decreases. The grain sizes of the more severely deformed samples were still smaller at temperatures only slightly above recrystallization.

If all were heated to about 800° C., the grain sizes would be approximately equal.

The history of recrystallization can be studied by subjecting strain-hardened metal to various temperatures and cooling and examining with a microscope after recrystallization has commenced but before it is completed. This has been done by Chappell¹ on iron, Mathewson and Phillips on Alpha brass, and Carpenter and Elam on aluminum. In all cases recrystallization begins at the old grain boundaries, preferably at the junction of three original grains. The new grains grow into the original grains with about equal ease.

Because new grains first appear at old grain boundaries, it is too commonly considered that new grains do not appear in the interior of the original grains. By referring to Fig. 35 and comparing it with Fig. 34 it will be obvious that many of the grains in the former must have formed in the interior of the old grains. A case which has been observed frequently is the recrystallization of coarse-grained tungsten after working. The original grains in a particular case were 0.25 in. in diameter. The ingot was worked below its recrystallization temperature about 50 per cent reduction in area and then heated quickly to a temperature well above that of lowest recrystallization. The grains then measured 0.008 in. in diameter. Most of the new grains were formed inside the original grains.

Compressed Powders.—Grain growth in the solid state in compressed metal powders has been studied most extensively with tungsten.² The metal does not consolidate until a temperature is reached far above that of recrystallization after severe cold work. In tungsten, the density of the compressed briquet is usually about 60 per cent that of the consolidated metal. The temperature at which the density becomes normal is about 2,400 to 2,600° C., which is at least 1,000° C. above the temperature of lowest recrystallization after severe cold working. After the briquet has consolidated, it consists of very small grains, which, however, are larger than the original particles of powdered metal. Higher temperatures normally produce larger grains, the same as in recrystallized metals. Special cases of abnormal grain growth in compressed tungsten briquets will be considered in connection with "germination."

¹ CHAPPELL, *J. Iron Steel Inst.*, No. 1, pp. 460-496, 1914.

² See note 3, page 99.

Obstruction.—Any foreign matter in a metal affects the grain growth characteristics. The foreign matter may be in solution in the metal, or it may be present as a mechanical inclusion or as a separate phase or constituent of an alloy. A good example of mechanical obstruction to grain growth is thoria (ThO_2), intentionally added to tungsten for the purpose of retarding the rate of grain growth or of producing smaller grains at any given stage in the life of a lamp. The effect of such obstruction is to introduce resistance to grain growth in approximate proportion to the amount of surface of the obstructing particles. A given amount of obstructing material therefore offers more resistance to grain growth, the smaller the particles or, with given sized particles, the greater the amount of obstructing material the greater will be the resistance to grain growth.

Thoria is introduced as thorium nitrate into the tungstic oxide before the latter is reduced by hydrogen to tungsten powder. The heating changes the thorium nitrate to oxide. Thoria is present in such small particles that they are not visible except under a high-powered microscope. With 0.75 per cent thoria present, a polished section may cut about 5,000 of these small particles per square millimeter.

Many cases of directional obstruction are encountered in worked metals. Slag in wrought iron sometimes obstructs grain growth more in a direction perpendicular to that of working than in the direction of working. When a tungsten briquet containing approximately 0.5 per cent thoria is sintered at a high temperature, the grains are, as nearly as can be measured, equiaxed. The thoria particles are also equiaxial in shape. When the metal is worked at a temperature near $1,300^\circ \text{C.}$, the thoria globules elongate into fibers which do not change materially when the metal is heated to a very high temperature. The tungsten grains developed in drawn wires containing thoria are nearly always longer in the direction of working than in other directions. It is obvious that threads of thoria will obstruct growth more in a perpendicular than in a parallel direction to their long dimensions.¹

¹ Although the thoria fibers are so small that they cannot be seen even with a high-powered microscope, their presence in fibrous form is indicated by the behavior of a coiled wire when the tungsten is removed by HCl at a dull red heat. The thoria remains in the form of the original coils. When unworked wire is treated with hot HCl gas, the thoria remains unattacked chemically, but is found after the treatment in a compact mass on the bottom of the boat or other receptacle.

Gradients.—The examples of grain growth given above are typical of the results ordinarily obtained and may be considered "normal" grain growth. Such growth usually results when the metal is reasonably uniform in structure and is uniformly heated. There are many instances of grain growth which seem to be in direct contradiction to the laws of normal growth. A careful study of these cases usually reveals that some non-uniformity either in structure or in temperature has been responsible for the apparent paradox.

The most important type of structural non-uniformity is that due to variable strain and may be referred to as a *strain gradient*. There are two types of strain gradient to be considered—"general" and "local." A *general strain gradient* consists in a gradual variation in the degree of strain over a considerable distance in the metal, such as is produced when a bar is bent or when a Brinell impression is made. A general strain gradient is the result of a grossly non-uniform mechanical deformation, but no deformation, however uniform, can be effected without introducing local variations in strain from grain to grain or in different parts of the same grain. These are referred to as *local strain gradients*.

A second type of structural non-uniformity consists in a non-uniform distribution of material which mechanically obstructs grain growth, and may be designated an *obstruction gradient*. Obstruction gradients are generally local in character.

Variations in temperature within a piece of metal are referred to as *temperature gradients*. Temperature gradients always exist during heating or cooling, and are greater the faster the change in temperature. The outside of a piece of metal is always hotter during heating than the inside, unless the heat is generated within the metal, as by the passage of an electric current, in which case the inside may be very much hotter. In ordinary muffle heating the rate is so slow that only small temperature gradients exist and, if the temperature distribution in the furnace is good, the metal may be considered substantially free from temperature gradients. When temperature gradients exist, they often play an important rôle in grain growth.

Certain combinations of non-uniformity of structure or temperature give rise to what may be termed "exaggerated grain growth"—that is, the production of grains of abnormally large size. Any case of the development of abnormally large grains

may be called *germination*.¹ The temperature range within which the abnormally large grains are formed is called the *germinative temperature range*.

Some typical examples of germination will be considered.

An important type of exaggerated growth was reported by Prof. A. Sauveur,² in soft steel containing about 0.05 per

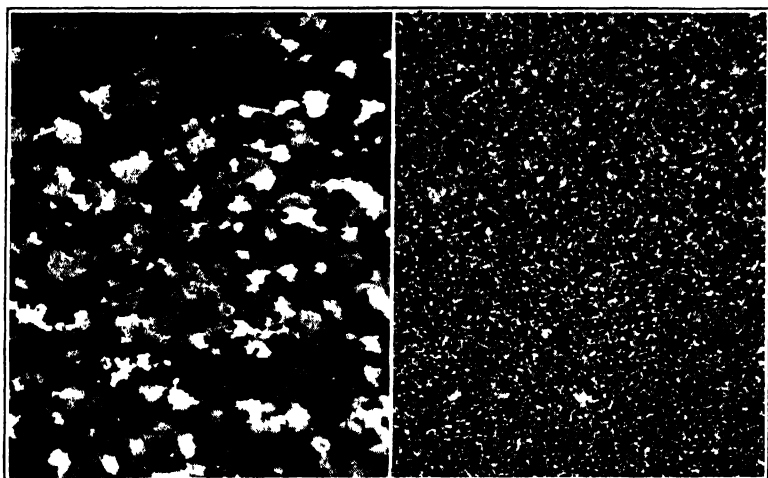


FIG. 50.—0.05 per cent carbon steel stressed cold to 40,000 lb. per square inch and then heated 7 hr. at 650° C. $\times 6$. (Sauveur.)

FIG. 51.—0.05 per cent carbon steel stressed cold to 38,000 lb. per square inch and then heated 7 hr. at 650° C. $\times 6$. (Sauveur.)

cent carbon, given a preliminary normalizing treatment by heating to about 900° C. and cooling in air. Test pieces were then subjected to definite degrees of strain by stretching in a tensile machine. Professor Sauveur expressed the strain in terms of the stress to which the specimens were loaded. This is not, of course, an accurate measure of strain, if materials of different stress-strain characteristics are being used, but where all experiments are carried out on the same material the stress does indicate the strain. A specimen stretched by a unit load of 40,000 lb. per square inch and then annealed for 7 hr. at 650° C. showed a marked increase in grain size (Fig. 50). A similar specimen loaded to 38,000 lb. per square inch and annealed in

¹ HOWE, H. M., On Grain Growth, *Trans. Am. Inst. Mining Eng.*, vol. 56, p. 582.

² SAUVEUR, A., "The Metallography and Heat Treatment of Iron and Steel," pp. 265-271

the same manner showed no grain growth, nor did germination result if the specimens were loaded to 42,000 lb. per square inch or more (Fig. 51).

Similar results are shown qualitatively by making a Brinell impression in a piece of mild steel and then heating it 7 hr.

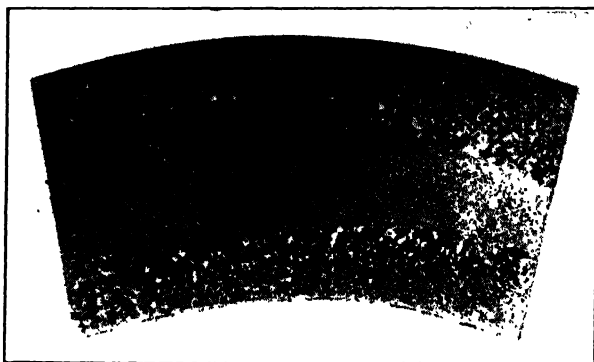


FIG. 52.—0.05 per cent carbon steel bent cold and heated 7 hr. at 650° C. $\times 6$.
(Sauveur.)

at 650° C. The strain is, of course, greatest immediately below the impression and decreases gradually as the distance from the impression increases. In a certain zone marked by coarse grains the strain is just right to produce germination.

Professor Sauveur bent another bar of mild steel cold and gave it the same heat treatment. Figure 52 shows how germination



FIG. 53.—Tapered bar of mild steel broken in tension and then heated to 870° C.
 $\times 5$. (Chappell)

took place in a certain zone between the axis and outside of the bar. Another very clear illustration of the facts is seen in Chappell's¹ tapered bar shown in Fig. 53. The strain increases continuously toward the small end of the bar. It will be noted that, as the degree of strain increases, the point at which grain growth begins is sharply marked. With still further strain,

¹ See note 1, page 105.

however, the grain size decreases in a gradual rather than abrupt manner.

Professor Sauveur concluded that there is a critical strain which produces germination. He was unable to produce marked grain growth in Armco iron containing only about 0.02 per cent carbon or in steels containing over about 0.12 per cent carbon. He reports:

"It would seem therefore that we must also recognize the existence of a critical carbon content (0.04 to 0.12 per cent) above or below which ferrite grains will not grow on annealing below the range, even if they have been critically strained."

The effect of carbon is undoubtedly one of mechanical obstruction to grain growth, so that, translating this last conclusion, it may be said that there is a critical amount of obstruction for exaggerated grain growth. It is now known that some coarsening will occur in steels containing less than 0.04 and more than 0.12 per cent carbon, but the maximum effect is obtained in the range named by Sauveur. It is also now recognized that "critical strain" applies to only one set of conditions as to annealing temperature and obstruction. For each degree of strain there is a critical temperature for germination.

This law is well illustrated by Ruder's results on silicon steel¹ (essentially a solid solution alloy). Pieces of silicon steel sheet were annealed at 1,100° C. and then subjected to various amounts of cold deformation by stretching. Pieces with each degree of strain were heated for 10 hr. at 750, 800, 950, and 1,100° C. The results are expressed qualitatively in Table V, where the amount of strain is expressed as per cent elongation. Only three degrees of grain growth are indicated. A blank space indicates that no growth has occurred. "Coarse" indicates very large grains, and "medium" indicates that some growth has occurred, but that the grain size is not so great as where "coarse" is reported.

Table V shows that the germinative temperature increases as the degree of strain decreases and that when the annealing temperature is well above the germinative temperature the grain size produced is smaller than with the same degree of strain, but an anneal at the germinative temperature. An additional fact not brought out in the table is that, as a rule, the grain size

¹ Discussion of papers "On Grain Growth" and "Grain Growth Phenomena in Metals," *Trans. Am. Inst. Mining Eng.*, vol. 56, p. 589, 1916.

produced at the germinative temperature is larger the higher the germinative temperature—that is, the less the strain. •

This series shows the effect of rate of heating through the germinative temperature on grain size. For example, in the 800° C. series, the 2.5 per cent elongation sample was at its ger-

TABLE V.—GRAIN GROWTH IN SILICON STEEL

Degree of strain, per cent	Annealing temperature			
	750° C.	800° C.	950° C.	1,100° C.
0.625	Coarse
1.250	Coarse	Medium
2.500	Coarse	Medium	Medium
5.000	Coarse	Medium	Medium	Medium
6.750	Medium	Medium	Medium	Medium

minative temperature. Consequently, in the 1,100° C. series the 2.5 per cent sample was heated rather rapidly through the temperature range around 800° C. and the grain size is smaller in spite of the fact that it was maintained 10 hr. at a temperature 300° C. higher. If the heating had been slow, or if the steel had been maintained at the germinative temperature a long time during heating to 1,100° C., the grain size could not have been smaller than in the 800° C. series, and might have been larger.

An example of exaggerated grain growth in tungsten was reported by one of the authors.¹ The normal grain growth-temperature curve for these tungsten briquets is shown by the straight line in Fig. 54. Exaggerated growth can be produced by using metal with a certain obstruction to growth and varying the temperature, at the same time maintaining a temperature gradient. Fine-grained tungsten powder containing 0.75 per cent ThO₂ was briquetted and heated to 2,600° C. by the passage of electric current, and held 30 min. The portion of the rod near the surface was very fine-grained, that at the axis somewhat coarser, and the intervening portion was very coarse-grained. The axis of the rod was the hottest and the surface the

¹ JEFFRIES, ZAY, Grain Growth Phenomena in Metals, *Trans. Am. Inst. Mining Eng.*, vol. 56, p. 571, 1916.

coolest. A briquet of this metal heated quickly to 3,200° C. develops a fairly uniform grain size throughout the briquet and only about one one-thousandth the size of that produced at 2,600° C.

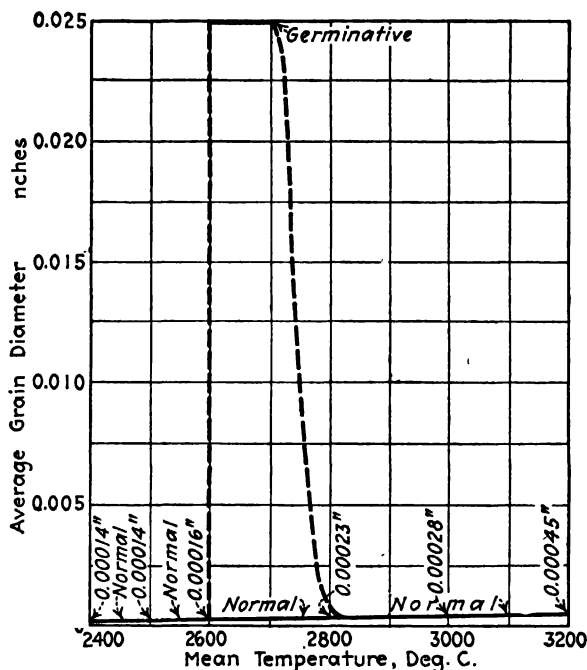


Fig. 54.—Grain size vs. temperature in tungsten briquet containing 0.75 per cent thoria.

The results of a set of tests on briquets made of very fine tungsten powder containing 0.75 per cent thoria are shown in Fig. 54. Between 2,600 and 2,800° C. there are two curves plotted, one marked "Germinative" and the other "Normal." The "Normal" curve was obtained with briquets of a separate lot of coarser tungsten powder containing 0.75 per cent thoria. Owing to the coarseness of the tungsten particles, no germination took place, and consequently the curve is normal. In the fine-grained powder the curve is normal up to 2,600° and above 2,800° C.¹ It will be observed that the grain size produced by

¹ Although the "normal" curves for the two grades of tungsten powder are somewhat different, the variations are not sufficient to indicate on the scale used for ordinates.

germination is of a different order of magnitude from the normal grain size.

Many variations in grain size can be produced in the fine-grained tungsten powder briquets by varying the rate of heating to temperatures above that of germination.¹ By heating very slowly to 3,200° C., for example, an average grain diameter of 0.03 in. was produced. By heating to 2,600° C. for 20 min. and then raising the temperature quickly to 3,200° C. and holding 10 min. an average grain diameter of 0.007 in. was produced. By heating quickly to 3,200° C. and holding 30 min. the average grain diameter was 0.00045 in. A study of the history of the formation of the large grains always reveals the fact that in the early stages a few grains reach a size considerably larger than their neighbors. Growth is relatively slow during this stage. As the large grains become larger the rate of growth increases, provided the smaller grains remain unchanged.

When germinative conditions are encountered, rapid heating to a temperature above the germinative range is often the surest and easiest way to prevent the formation of large grains. In the few cases where large grains are desired the rate of heating is again all important.¹

Germination can be produced in tungsten powder by incorporating the proper amount of obstruction matter (thoria) and heating to a certain temperature by the passage of electric current. Six lots of tungsten powder were prepared containing 0, 1, 2, 3, 4, and 5 per cent thoria. These were briquetted and heated for 12 min. in an atmosphere of hydrogen at 3,200° C. by the passage of electric current. A temperature gradient obtained from the axis (hottest portion) to the surface of the briquet. The resulting grain sizes produced are shown graphically in Fig. 55. Although the obstruction to grain growth is greater the greater the amount of thoria, there is a critical combination of obstruction, temperature, and temperature gradient which produces a germinative condition. This series is particularly important, because it shows how the germinative temperature may be made non-existent by raising it hypothetically to a temperature above the melting point of the metal. The 5 per cent thoria sample can actually be melted without first producing large grains.

¹ See note 3, page 99.

Another case of germination in drawn tungsten wire is very interesting.¹ The tungsten metal in question has a small amount of non-metallic obstruction in very small particles. The wire was drawn in the usual way, so that the strain hardening was very great. If this wire is heated quickly to a temperature near the melting point of tungsten, a small grain size is pro-

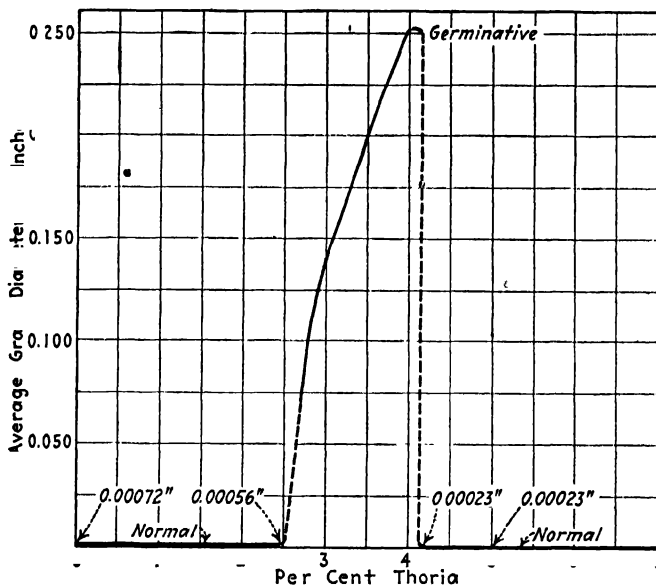


Fig. 55.—Effect of thoria on grain size of tungsten.

duced. If, however, the temperature is raised gradually by means of an electric current, the structure is very coarse. In fact, the grains usually extend across the whole cross-section of the wire and may be as much as 0.5 in. in length. These large grains form in a time not exceeding about 10 sec. This coarse-grained structure is desirable in certain lamps to prevent undue sagging at high temperatures.

Germinative conditions are not confined to the growth of grains completely in the solid state. The present authors have found that mechanical obstruction introduced in slight amount into a liquid aluminum alloy containing 4 per cent copper produces a moderate refinement of the grain. When introduced in certain greater amount, the grain size after solidification is very

¹ See note 3, page 99.

large. With still greater amounts of obstructing material the grain size again becomes small. The rate of freezing was the same in all of the tests and the only variable was the amount of obstruction material. Enlarged photographs of this series are



FIG. 56.—Aluminum alloy containing 4 per cent copper cast in sand mold. $\times 5$.

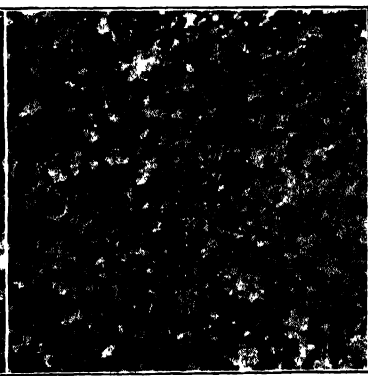


FIG. 57.—Aluminum alloy containing 4 per cent copper plus a small amount of material to obstruct grain growth. $\times 5$.



FIG. 58.—Aluminum alloy containing 4 per cent copper with more obstructing material than in Fig. 57. $\times 5$.

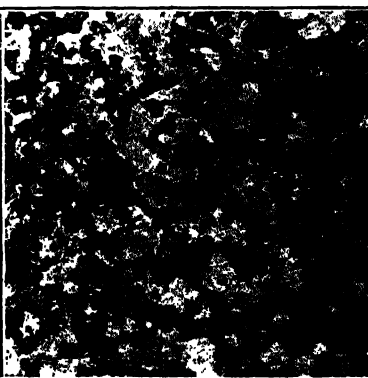


FIG. 59.—Aluminum alloy containing 4 per cent copper with more obstructing material than in Fig. 58. $\times 5$.

shown in Figs. 56 to 59. Because of the "coring" tendency during freezing of solid solution type alloys, a "concentration gradient" might exist. A concentration gradient would produce a freezing temperature gradient which might promote the formation of large grains. In the examples just considered,

however, the concentration gradient by itself was not sufficient to produce germination; a certain amount of obstruction was necessary. The same amount of obstruction did not cause germination in commercially pure aluminum. The striking resemblance of the 4 per cent copper series, at least qualitatively, to the series in which the thoria content was varied in tungsten will be noted.¹

Germination may also be produced by a temperature gradient in a severely strained metal or in iron passing through the allotropic transformation. A condition of grain size contrast which leads to germination may also develop in a severely strained metal on heating above the recrystallization temperature. In this connection it has been observed that germination often follows the first structural changes on heating. For example, a strained metal may recrystallize normally and the recrystallized grains may, at a little higher temperature or on longer exposure, coalesce to form abnormally large grains. In cases of germination due to obstruction and temperature gradients there may be some growth below the germinative temperature.

One method of utilizing the principles of grain size contrast and temperature gradients to produce excessively large grains has been described by Ruder for silicon steel² and Schaller for tungsten. Ruder has treated a strip of silicon steel about 1 by $\frac{1}{16}$ by 14 in. in such a manner that it consists mostly of a single grain. Schaller has produced some grains about 7 in. long in tungsten wire of small diameter. The process consists essentially in starting with a material with grains so small that much growth takes place on heating. A small area of the piece of metal is heated to a high temperature in such a manner as to develop large grain locally. The piece of metal is then moved through the heated zone at a rate comparable to the rate of absorption of the small grains by the large.

Macromechanism of Grain Growth.—Grain growth in the solid state takes place by the gradual absorption of some of the grains by others. This may be referred to as "boundary migration." It was formerly held by some metallographists that whole grains gradually changed orientation until two adjacent ones

¹ JEFFRIES, ZAY, Grain Growth in Metals, *J. Inst. Metals*, No. 2, p. 109, 1918.

² *Trans. Am. Inst. Mining Eng.*, vol. 47, p. 569, 1913; *J. Ind. Eng. Chem.*, vol. 5, p. 452, 1913.

had the same orientation, after which they suddenly merged. The boundary did not move, according to this view, but disappeared as a boundary on account of the common orientation.

Rosenhain long ago showed that growth in lead took place by boundary migration. One of the present authors¹ reported the results of an investigation showing conclusively that growth in iron took place by boundary migration. Carpenter and Elam² have described a most satisfactory method for studying the progress of grain growth in a tin alloy containing a small amount of antimony. When this alloy is etched and heated into the grain growth temperature range and then cooled to room temperature, the original grain boundaries as well as the new boundaries are visible. Inasmuch as each heating and cooling reveals the new boundaries and does not efface the old ones, as many sets of boundaries as desired can be obtained. Photographs taken after each heating give a splendid record of the history of growth. Carpenter and Elam's results give additional proof that growth takes place by boundary migration.

Laws of Grain Growth.—1. The grain size of cast metals is usually smaller the more rapid the rate of solidification.

2. The grain size in cast metals which undergo no phase change in the solid state cannot be changed appreciably by heating below the melting point.

3. Grain growth in the solid state may occur in (a) worked metals, (b) compressed powders, (c) electrodeposited metals, (d) in iron when it changes allotropic form, and (e) in alloys in which a new phase is formed in the solid state.

4. The recrystallization temperature is lower (a) the greater the amount of deformation, (b) the smaller the grains prior to deformation, (c) the purer the metal, (d) the lower the temperature at which the deformation is effected, and (e) the longer the time of heating.

5. In any given metal the grain size, after complete recrystallization, is normally smaller the lower the recrystallization temperature.

6. Above the recrystallization temperature the grain size is normally greater the higher the temperature and the longer the exposure.

¹ See note 1, page 116.

² See note 1, page 100.

7. The higher the temperature the more rapid the grain growth. At a temperature near the melting point, a few seconds is often sufficient to produce grains which may not change further on extended exposure.

8. Certain conditions of non-uniformity sometimes give rise to the formation of abnormally large grains. This is called "germination."

9. The non-uniformities giving rise to germination are grain size contrast, strain gradients, temperature gradients, concentration gradients, and obstruction gradients.

10. The presence of foreign matter or a second phase introduces mechanical obstruction to grain growth. Resistance increases as the quantity of foreign matter or other phase increases and as the particle size decreases.

11. The presence of a certain amount of obstruction matter promotes germination.

12. The higher the germinative temperature the larger will be the grains and the quicker will they form.

13. The more rapid the heating through the germinative temperature range, at least within limits, the finer will be the grain size.

Need of a Working Theory.—The material so far presented in this chapter has consisted entirely in the presentation of the facts of grain growth and of such generalizations as may be drawn from them. Some of these statements may require correction or amendment in the light of more accurate or more complete observations, but in the main they are well established and are of immediate practical use in controlling grain growth in metals.

It is also desirable to have a conception of the fundamental causes underlying these phenomena, as by this means the various facts can be more easily correlated and new facts more rapidly discovered. Many contributions have been made to the literature on grain growth and no small part has been devoted to the theoretical aspects. Naturally, many of the ideas have been discarded and certain ones have gained a sufficient following to warrant their general acceptance by metallographists. In the remainder of this chapter the authors will put forth a conception of the fundamental causes of grain growth consistent with the observed facts and with modern developments in molecular physics.

Possible Causes of Grain Growth.—Grain growth obviously results from the tendency of matter to assume the form of greatest physical stability, which is the form of least energy. The crystallization of metals from the liquid state is always accompanied by an evolution of heat, representing the loss in the kinetic energy of the atoms incident to their fixation in the rigid crystal lattice. The atoms at the surface of a liquid or solid body are less subject to the attraction of their neighbors than are the atoms in the interior. They are therefore more free to move and consequently possess more energy of motion. A "free" surface of any body is thus a locus of extra energy, known as "surface energy" or sometimes "surface tension." There is, therefore, a tendency for small particles, such as drops of a liquid or crystals of a solid, to unite to form larger particles, since in so doing they diminish their surface area and hence their total energy. It follows that the most stable form for any piece of metal would be a single crystalline grain.

To have the smallest possible surface area, this grain should be spherical in shape. This would not, however, necessarily give the minimum surface energy, because of the geometrical properties of the crystal. The most stable shape for a crystalline substance is often an idiomorphic form built up of the natural crystal faces. On the other hand, it is well known that small particles of certain crystalline constituents in a metallic aggregate tend on long heating to assume a spherical form. The question is not of great importance here, and may be dismissed by saying that the most stable form of a metallic crystal is that of least surface energy, which will probably be either idiomorphic or spherical.

There has been considerable confusion in the literature on grain growth, arising from a lack of distinction between true or stable equilibrium and metastable equilibrium. Some have considered that the ultimate stable condition of a piece of metal is not a single crystal, simply because such specimens are very rarely encountered, and then only as a result of rather special manipulation. Such a conclusion is just as absurd as a conclusion that the gravitationally stable form of the earth's surface consists of mountains and valleys, and for the same reason. Grain growth is a process involving inertia which must be overcome, just as the friction of the material composing a mountain must be overcome before the force of gravity can level it

with the plain. Similarly, the fact that, even after prolonged annealing above the recrystallization temperature, grains may be found having jagged or irregular outlines does not in any way disprove that smooth outlines would represent a condition of greater thermodynamic stability.

Obviously, any roughness on the surface of a crystal is a source of increased surface energy, and hence diminished stability.

If a crystal is subjected to an external load below its elastic limit, it becomes temporarily deformed or distorted. On release of the load, the crystal returns to its original form. The deformation of the crystal by the external load requires an expenditure of energy which is stored in the crystal itself and manifested by its ability to return to its original shape, doing work as it returns. An elastically deformed crystal thus contains more energy than a similar crystal free from stress and distortion, and is therefore less stable thermodynamically.

All the factors have now been considered briefly, which, according to present knowledge, may influence the stability of a crystal—namely, size, form, surface, and distortion. The most stable form for a solid metal is a single crystal, spherical or idiomorphic in shape, of smooth surface, and free from any distortion of its space lattice. All solid metals must tend to assume this condition.

Conditions for Grain Growth.—Any piece of metal which consists of more than one grain must possess a tendency for grain growth which is greater in proportion to the departure from the condition of maximum stability. For convenience, this tendency may be designated *growth force*. Grain growth will take place whenever the growth force is sufficient to overcome the opposition to growth. Grain growth takes place by a process of boundary migration which involves the gradual transfer of atoms from the lattice of one grain to that of the adjacent grain. Whether or not this transfer takes place through a layer of amorphous grain boundary metal, it requires a certain degree of atomic mobility or *temperature* for its accomplishment. There is usually present in metals some form of obstruction which mechanically interferes with grain growth, such as thoria in tungsten and pearlite in steel. This obstruction may be so great that it prevents grain growth altogether. In any case, with a given growth force, the presence of obstructing materials raises the temperature required for grain growth.

It has been suggested that, in order for one grain to absorb another, it is necessary that the orientations of the two grains be very similar. Some observers have reported, however, that the relative orientation of the grains has no apparent effect on growth. It may well be imagined that, although similarity of orientation might facilitate the process of growth, this very condition would also decrease the force tending to cause growth. In any event, there is not sufficient evidence to justify consideration of relative orientation as a factor in grain growth.

The proposition that the impetus or growth force is due to a condition of thermodynamic instability and that, when such a condition exists, growth will take place whenever the temperature and obstruction factors permit may be taken as a sound foundation for the development of a theory of grain growth. The factors affecting the stability of the grains of a metal, and hence the growth force, have been indicated (size, shape, surface, and distortion). The relative importance of these factors will now be considered more fully.

Shape and Surface of Grains.—There are frequently found, even in unstrained metals, grains of such elongated or extended shape that the ratio of surface area to volume is abnormally high for grains of that size. Presumably, such grains are less stable than grains of the same size but of more nearly equiaxed shape, which, therefore, tend to grow at the expense of the former. Actual observation indicates, however, that such differences in shape constitute a relatively minor factor in grain growth.

Rosenhain has observed that in deformed lead, in which grain growth was occurring, the outlines of the grains were ragged, while in cast lead, in which grain growth could not be produced by heating, the outlines of the grains were much more smooth. He considered that the ragged boundaries represented a condition of greater surface energy, hence less thermodynamic stability, and, consequently, a greater tendency for grain growth. This may account, in part, for the fact that grain growth occurs in worked metals but not in cast metals. General observations on the effect of grain outline or surface on grain growth phenomena are lacking, however, so that this factor cannot be incorporated as basic in a theory of grain growth.

Grain Size the Important Factor.—The tendency of metals to reduce their store of energy by increasing their grain size is the factor which has probably been considered the principal cause of

grain growth. There are, nevertheless, many who do not regard this as furnishing an adequate explanation of all the phenomena involved. The authors believe that grain size, considered both absolutely and relatively, is the chief factor determining the growth force or tendency for grain growth to occur, and that it furnishes the basis for a completely satisfactory theory of grain growth.

A crystalline grain is to be regarded as an organized structure having a definite power to hold its atoms in their positions in its space lattice, and to attract neighboring atoms into its lattice. This power is due to the cumulative effect of the directional force fields of the atoms composing the grains. The exact nature of these force fields is not known, consequently the manner of their linkage is unknown. It is held by some students of atomic and molecular physics that the attractive force of an atom does not extend to a distance of more than 2 or 3 atom diameters, in which case the orienting power of a crystal would be very little affected by its size when such a crystal contained more than about 6 atoms across its smallest diameter. The authors believe that the influence of the atoms within a crystal upon its orienting power extends to a much greater distance. In any event, it is certain that large crystals or crystalline grains do possess that property which has here been called "orienting power" to a greater extent than do similar crystals of smaller size.

Many examples of this general fact are known. It is known that the solubility of many salts in water is greater the finer the particles of the salt. Some figures for the solubility of calcium sulphate in water are as follows:

	DIAMETER OF GRAINS	
	2 μ	0.3 μ
Solubility per liter grams.....	2.08	2.56

That is, the concentration of a saturated solution in equilibrium with an excess of the solid salt is greater the smaller the particles of the solid. This can mean only that the small particles are less capable of attracting atoms or molecules from solution than are the larger particles. The actual observed effect upon the solubility is small, and is smaller the larger the size of the particles of excess solid. It is sufficient, however, to cause the size of the particles or crystals to increase by a process of solution and redeposition. Chemically speaking, the solution is unsaturated with respect to the smaller crystals but supersaturated

with respect to the larger crystals. The former therefore dissolve and the material thus removed precipitates upon the larger crystals.

Entirely similar phenomena are observed in metals. The most familiar example is that of cementite (iron carbide) in iron. If a steel containing, say, 0.90 per cent carbon is hardened by quenching in water from about 760° C. and then tempered by reheating to about 400° C., it is obtained in a structural condition which is metallographically termed "troostite." Although the structure of troostite is irresolvable under the microscope, it is quite certain that it consists of submicroscopic crystalline particles of cementite imbedded in ferrite (iron). Now, if the steel is heated for several hours at a temperature of about 700° C., the cementite particles become visible, and on continued heating can be observed to grow. They are not directly connected with each other in any way, so the transfer of material from one particle to another must take place through the ferrite. The smaller particles dissolve in the ferrite until a solid solution is formed which is supersaturated with respect to the larger particles. Precipitation then occurs on these larger particles, with the net result that they grow at the expense of the smaller particles. Physically, this means that the larger particles have stronger attractions for their constituent atoms than do the smaller particles.

The general principle here illustrated is that, in an aggregate of grains of various sizes, the larger grains tend to grow at the expense of the smaller. If a condition is assumed in which all of the grains are of exactly the same size and similar in other respects, there is a balanced condition with no opportunity for grain growth, even though the tendency for growth is present, due to the fact that the thermal stability of the aggregate would be increased by an increase in grain size. The grains all possess equal powers of orientation, however, so that there is no resultant growth force. Grain growth thus depends on a *difference* in grain size, or on what may be called "grain size contrast."

While the orienting power of a crystal probably increases with its size almost indefinitely, there is ample evidence that the rate of increase is most rapid when the size is very small, and may become practically negligible for larger crystals. Thus the effect of crystal size on the solubility of salts is appreciable only for relatively small crystals. Similarly, the growth of cementite particles in steel becomes very slow after they have reached a

diameter of about 0.00004 in. The actual extent to which such growth proceeds is determined largely by the temperature, since a higher temperature is necessary to facilitate growth when the growth force is small.

Meissner¹ has recently determined the effect of particle size upon the melting point of myristic acid and found that this temperature is lowered about 0.5° C. by decreasing the particle size from 10 to 0.8 μ . This phenomenon is another illustration of the fact that very small particles of solid have less attraction for their atoms or molecules than do larger particles.

The growth of certain grains in a metallic aggregate at the expense of others may be regarded as a competitive process. At the boundary between two adjacent grains there is a competition for the surface atoms, or the atoms of the essentially amorphous cement which probably surrounds the grains. The grain which has the greater orienting power attracts atoms from the other grain and thereby grows. Drawing an analogy with vital processes, it may be said that the grains have definite powers of attack and defense, and that the stronger grains feed upon the weaker. Power of attack and of defense is, of course, synonymous with what is here called orienting power. Orienting power depends upon grain size. The tendency for growth, or the growth force, depends upon a difference in orienting power. This difference increases with the disparity in grain size and with the smallness of the smaller grain.

To sum up the above discussion, the causes favoring grain growth are:

1. Small grain size.
2. Grain size contrast.

The importance of grain size contrast as a cause of growth has been questioned by some students of the subject and has recently been emphatically denied by Carpenter and Elam² as a result of observations purporting to show the absorption of large grains by small ones. These observations are open to two serious objections:

1. They were made on plane sections, and grains which appear small on such a section may actually be very much larger. Given

¹ MEISSNER, The Influence of State of Division on the Melting Point, *Z. anorg. Chem.*, vol. 110, pp. 169-186, Mar. 12, 1920.

² CARPENTER and ELAM, Crystal Growth and Recrystallization in Metals *J. Inst. Metals*, No. 2, 1920.

any two adjacent grains, of which one is only moderately larger than the other, it will usually be possible to pass through them a plane on which the sections of the grains are reversed in size. It is therefore a mathematical probability that when the differences in grain size are not great there will be on any section including a large number of grains some cases where the larger grains appear to be the smaller. In the discussion of Carpenter and Elam's paper, this objection was raised and has not been satisfactorily answered.

2. The alloy of tin and antimony used in their experiments is very soft and susceptible to strain in the polishing operation. It is therefore quite possible that an observed large grain, apparently intact, had actually been broken up into very much smaller fragments. There is no reason why a small unstrained grain should not absorb a large strained grain; this is, in fact, more probable than the reverse phenomenon.

The present authors do not know of any well-established case of the absorption of a large unstrained grain by a smaller grain. Even if some such cases should be established, however, they would merely show that some of the other factors which have been mentioned may occasionally overbalance the grain size contrast factor, and would furnish no basis whatever for the dogmatic statement that grain size contrast is not important as a cause of growth. On the other hand, there is abundant positive evidence of the strongest kind that the grain size contrast principle is important and usually dominant.

Temperature and Obstruction Limiting Conditions.—The presence of a growth force due to the causes just described will not result in grain growth if the temperature is too low or if the mechanical obstruction to growth is too great. The factors are mutually interdependent. With given conditions as to mechanical obstruction, grain growth will occur at a lower temperature the greater the growth force; or, conversely, the less the growth force the higher the temperature required to bring about grain growth. With a given growth force the temperature required to bring about growth increases with the amount of mechanical obstruction. Thus grain growth is controlled by three factors: (1) *grain size*, relative and absolute, which determines the growth force or tendency for growth to occur; (2) *temperature*, which is equivalent to atomic mobility and determines whether the growth force can overcome the rigidity of the metal; and

(3) *obstruction*, which mechanically hinders and sometimes entirely prevents grain growth.

Metastable Equilibrium.—Grain growth may fail to occur or, having started, may come to a halt as a result of unfavorable conditions in respect to any one of these three factors. The growth force may be so small that, even in the purest metal, grain growth will not occur at any temperature short of the melting point. This is the condition that ordinarily obtains in metals solidified from the molten state and not subjected to any form of deformation. It is quite natural that this should be the case, in view of the rapidity of grain growth at temperatures near the melting point. The short time which elapses during even the most rapid solidification is sufficient for the growth force to be reduced by the process of grain growth to such a point that no further growth will take place at lower temperatures, even when maintained for long periods of time.

It is quite common to find fairly marked grain size contrast in cast metals in which it is not possible to bring about grain growth. A common example is found in ingots at the junction of the columnar grains which grew out from the mold walls with the equiaxed grains in the central portion of the ingot. Such observations have been considered by some to be inconsistent or even incompatible with the grain size contrast principle. While granting that the failure to obtain grain growth under these conditions may be influenced by the shapes of the grains or their contours, the present authors consider that the grain size principle alone is sufficient to account for the facts. While the grain size contrast may in some of these cases be considerable, the actual grain size is never very fine, in comparison to the grain size of worked metals. It is this general coarseness of grain in cast metals to which may be attributed their failure to exhibit grain growth on heating at temperatures below the melting point.

There is reason to believe that grain growth, in the solid state, does occur in cast metals during the process of solidification. An example was described earlier in this chapter of a tungsten rod, the axial portion of which had been melted by an electric current and then allowed to resolidify. It was pointed out that, whereas it might be expected that the grains formed during resolidification, would be found starting from the unmelted grains as nuclei, what is found in fact is that the new central grains are vastly larger than the old grains in the outer rim, ex-

tending from this rim to the center of the rod. It is quite certain that, in the initial stages of the resolidification, the new grains actually did form upon practically all of the old grains in the rim and began to grow inward. The final result indicates very strongly that some of the larger grains absorbed their smaller and already solidified neighbors.

Upon annealing worked metals under certain conditions, it has been shown that the final grain size depends very largely upon the annealing temperature. For the lower annealing temperatures the grain size depends to a large extent upon the degree of prior strain hardening, the rate of heating, time of holding at heat, etc., but at higher temperatures the effect of such variables is greatly reduced, especially if the metal is fairly free from growth obstruction, so that the annealing temperature is the principal factor determining the grain size. In other words, there is an apparent equilibrium grain size for each temperature. As the temperature of the metal is raised, grain growth takes place until the growth force is reduced to a point where it can no longer cause growth under the existing conditions of temperature and obstruction. The metal is then in a state of metastable equilibrium as regards grain growth. In this condition the grains are usually fairly equal in size. Consequently, the normal grain growth which takes place on heating a worked metal consists merely in a change of structure toward the condition of metastable equilibrium for the temperature of the anneal.

Recrystallization is Grain Growth.—The replacement of a single strained grain by a number of unstrained grains of various orientations suggests that new crystalline nuclei are formed during the process of recrystallization. It is known, however, that the strained grain has within it an abundance of nuclei in the form of fragments produced by deformation. It is more logical to suppose that recrystallization consists in the growth of some of these grain fragments to visible size than that entirely new nuclei are formed. A strained grain may be regarded as an aggregate of a large number of crystalline fragments, each equivalent to a very small grain. This aggregate is not the same as an equal number of unstrained grains of similar size in annealed metal, since the boundary conditions are undoubtedly different. It is probable, too, that the change in orientation from fragment to fragment is very slight as compared with that from grain to grain in an annealed metal. In spite of such differences, the strained

grain is actually an aggregate of smaller grains which, because of their small size and the size contrast unavoidably present, are especially susceptible to growth on heating.

When an annealed metal is plastically deformed, the action is most severe near the grain boundaries. The grain fragments formed are, therefore, smallest in these regions. Small grain size is conducive to growth at low temperatures, and it is therefore quite natural to find, on heating a strain-hardened metal under conditions of time and temperature which produce only partial recrystallization, that the new grains are first observed at the old grain boundaries. Long heating at low temperature might cause these first grains, by reason of their advantage in size, to absorb all of the grain fragments in the central portion of the old grain. In such a case the new grains could not possibly be smaller in diameter than one-half the least diameter of the strained grain. If the metal is heated quickly to a temperature well above that of incipient recrystallization, fragment growth will take place substantially at the same time in all parts of the old grain. This is probably what happens in ordinary industrial annealing.

An objection to this view that recrystallization is merely sub-microscopic grain growth is found in the belief held by some that during plastic deformation the grain fragments retain substantially their original orientation.¹ It is a fact that the new grains which form from a strained grain upon proper heating have orientations which may differ from that of the original grain. If these new grains are held to have grown from the fragments of the old grain, then it must be considered that the fragments which acted as nuclei also possessed different orientations.

In view of the fundamental importance of the question, some experiments were made by means of *x*-ray analysis to determine whether or not new orientations are produced by deformation. The methods and results have been published.² The evidence was conclusive that new orientations are produced by the simplest types of deformation, such as rolling or pressing. A striking illustration of change of orientation produced within

¹ MATHEWSON and PHILLIPS, Recrystallization of Cold-worked Alpha Brass on Annealing, *Trans. Am. Inst. Mining Eng.*, vol. 54, p. 608. After considering the various ideas on this subject these authors conclude that probably new orientations are produced by plastic deformation.

² BAIN and JEFFRIES, Mixed Orientation Developed in Crystals of Ductile Metals on Plastic Deformation, *Chem. Met. Eng.*, vol. 25, No. 17, pp. 775-777, Oct. 26, 1921.

a grain by twisting is shown in Fig. 60. The definite proof that the grain fragments produced by the deformation of a single grain actually have mixed orientations removes the only valid objection to the view that recrystallization is merely grain growth.



FIG. 60.—Single crystal of tungsten twisted cold, polished, and etched. $\times 200$. (Tarasov.)

The actual amount of grain growth involved in the process of recrystallization is remarkably great considering the small change in temperature necessary for its accomplishment. The average grain diameter in a pure metal or solid solution alloy which has just been completely recrystallized is generally not less than about 0.0005 in. As yet there is no means of accurately measuring the fragment size in a strain-hardened metal, but it is known that it is very small, since it requires only a slight deformation to produce slip bands upon a polished metal surface so close together that they cannot be resolved under the microscope. The much more severe deformations commonly effected in cold-working operations must produce fragments with diameters on the order of 0.000001 in. The increase in grain diameter during recrystallization is then about 500 to 1. In terms of grain volumes the increase is 125,000,000 to 1. The same ratio represents the decrease in the number of grains in a given volume of metal. Expressed in a slightly different way, 125,000,000 grain fragments unite during recrystallization to form one unstrained grain. The temperature change required to bring this about for ordinary periods of heating is usually not over 150° C.

¶ If a similar ratio of grain growth were effected in the recrystallized aggregate whose grains average 0.0005 in. in diameter, the new grains would be $\frac{1}{4}$ in. in diameter. This is an enormous grain size for any normal worked metal. Such grain sizes are frequently obtained under germinative conditions, but seldom as a result of normal grain growth, even on raising the annealing temperature from that of recrystallization to just under the melting point. This suggests that the commonly observed recrystallization normally takes place under what might be called germinative conditions.

It has been seen that the recrystallization temperature is higher the less the previous strain hardening. As a cause of grain growth, strain is merely a mechanical process of grain refinement. The greater the degree of strain the smaller are the grain fragments produced and, consequently, the lower the temperature at which grain growth, or recrystallization, will take place.

Desch and others have examined the shapes of whole grains removed from cast metals and from worked metals which had been heated to high temperatures. The shapes were as nearly spherical as could be expected when it is considered that the grains were in contact with other grains on all sides, and hence completely filled the space. Foam cells, when isolated, are spherical, but assume polyhedral shapes when a large number completely fill a certain space. The external shapes of grains have been found to be very similar to those of foam cells. As evidence of the effect of surface forces, the smaller grains in an aggregate are usually more nearly spherical in shape than adjacent larger grains—the boundaries of the smaller grains tend to be convex. The number of faces on the surface of the polyhedral grains varies somewhat, but on the average there are 12 to 15 faces. These polyhedral shapes may be considered as the stable shapes toward which grains change when free growth conditions are possible.

The grain fragments produced by cold work are bounded by crystallographic planes: Inasmuch as most of the deformation takes place by movement along a relatively small number of types of slip planes, it would be expected that cold-worked metal would consist of fragments of entirely different shape from the grains produced by grain growth. In general, the crystal fragments of cold-worked metals will depart much more from

spherical shape than grains which have been allowed to form at relatively high temperatures by grain growth. In this respect, crystal fragments of cold-worked metals are only in part similar to very small grains in an unworked metal. The changes which take place on heating a cold-worked metal below the recrystallization temperature would be largely in the direction of perfecting crystalline organization at the boundaries between crystal fragments and perhaps in the coalescence of some of the very smallest fragments. Such structural changes would be accompanied by moderate changes in physical properties. Complete recrystallization, however, would involve not only a reduction in the number of crystal fragments, but the growth of these under such conditions that the external shapes of the new grains are no longer controlled by crystallographic planes (slip planes) but by the surface forces between grains of characteristic polyhedral shape. Recrystallization is, therefore, not merely decrease in number and increase in size of crystal fragments, but it represents a change from grain fragments—which owe their external shapes to the slip planes—to grains whose external shapes are controlled by surface tension forces.

It has been stated above that normally no new nuclei form on recrystallization. X-ray analysis has given the best evidence on this point. When metals are cold worked very severely, there is a tendency for the crystal fragments to become oriented in definite directions with reference to the direction of working. After the working has progressed a considerable amount, certain orientations are found to be entirely absent in the cold-worked metal. When such a metal is heated above the recrystallization temperature, the new recrystallized grains have the same directional orientation as the crystal fragments in the cold-worked metal. If new crystalline nuclei formed on recrystallization, they would be expected to form with random orientations.

It is very important here and subsequently to keep clearly in mind the fact that small grains or fragments facilitate growth because they are easily absorbed. In an aggregate of grains which are strained to various extents, the grains which are *least* strained are in a position to grow by feeding upon their more severely strained—*i.e.*, fragmented—neighbors. It has been a common mistake to consider that, since strain leads to grain growth, the grains which are most strained are the ones which grow.¹ This fallacy seems to be based upon a false conception of

¹ See note 2, page 124.

the energetics of the case. It is held that energy is required to impart the power to grow, and that this energy must be stored in some way in the grain. The strained grain is, therefore, regarded as the one endowed with the power of growth. Actually, the conditions are the exact reverse. The unit which does the growing is the grain of greatest thermodynamic stability, and hence *least* energy content. The logic of this is apparent on considering the conditions on the solidification of a metal from the molten state. The solid, unstrained grains feed upon the molten phase, which has the higher energy content.

Grain Growth in Electrodeposits.—According to the conditions of deposition, electrolytic metal may be obtained in a soft, coarse-grained variety or in a hard form whose structure is so confused that Beilby was led to the conclusion that it is amorphous. Any gradation between these two extremes may also be obtained. If the harder varieties are annealed, they are found to have “recrystallized” very much after the manner of strain-hardened metal. Beilby attributed this to the formation of crystalline nuclei in the amorphous metal. Later researches have shown that the hard electrodeposited metal is predominantly crystalline. There is little doubt that the hardness and recrystallizing properties are due to a very small grain size, just as they are in strain-hardened metal. It is sometimes said that the metal is deposited in a “state of strain,” which is correct if taken to mean a condition similar to that produced by plastic deformation. The essential feature in this state of strain is the great fineness of grain.

Metal Powders.—Growth phenomena in metals formed from powders are exactly the same as in metals which have been melted and cast, although some writers would place them in a separate class. It has been erroneously stated that metal powders will not sinter to form a coherent mass when heated unless the pressure is sufficient to cause fusion at the temperature used. As a matter of fact, tungsten powder can be sintered below the melting point with no pressure except that due to its own weight. In fact, it is very difficult to see how pressing a metal powder briquet could have any effect on the melting point except to raise it.

The particles of powder used in making tungsten briquets are crystalline grains formed by reduction from tungstic oxide. It is possible that, when strongly compressed, some of these grains

are plastically deformed. Any such strain hardening should be removed before sintering takes place, as the sintering temperature is far above that of recrystallization. Sintering therefore consists in the union of unstrained grains accompanied by such boundary migration as is necessary, and usually by distinct grain growth. The grain size of a sintered ingot is never less than the size of the particles from which it was formed. Grain growth here is due to the usual causes—namely, grain size contrast and initial fineness of grain.

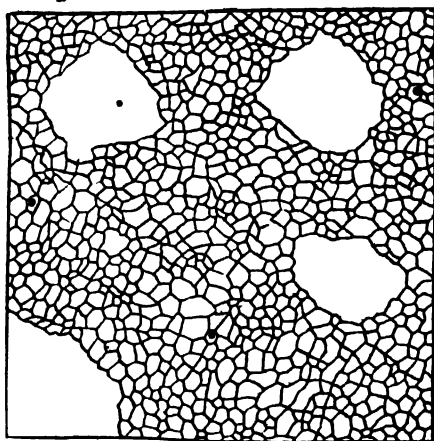


Fig. 61.—Metal with moderate grain size contrast.

Germination.—Consider the conditions of grain growth in the hypothetical case represented in Fig. 61. The small grains are supposed to be nearly alike in size, but sufficiently different to give rise to a growth force capable of causing grain growth when the metal is heated to a suitable temperature, which will be designated T_2 . The small grains in contact with the few large grains are similar to those in the interior of the fine-grained regions. The growth force is therefore much greater at the boundaries of the large grains than in the interior of the fine-grained regions and the large grains will grow at a lower temperature, T_1 . Now suppose the metal is heated to a temperature above T_1 but below T_2 . The few large grains will grow at the expense of the small grains until the latter are entirely absorbed and the large grains finally meet one another. Grain growth will then cease on account of the great resistance of the large grains to absorption, and the resulting condition is represented in Fig. 62.

Suppose that, instead of being heated to between T_1 and T_2 , the metal is quickly heated to a temperature above T_2 . The large grains will then begin to absorb the small grains as before,

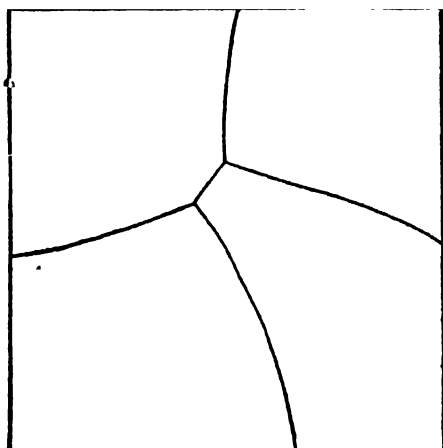


FIG. 62.—Metal shown in Fig. 61 heated so that large grains absorb all of small grains.

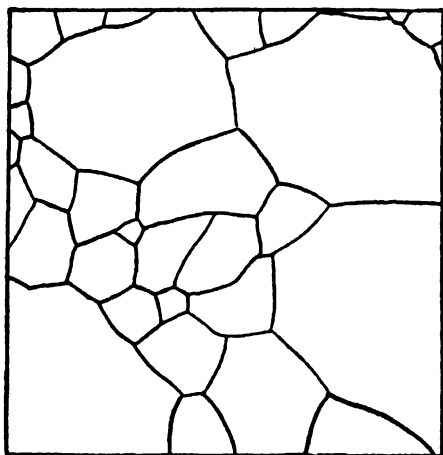


FIG. 63.—Metal shown in Fig. 61 heated so that some of the smaller grains are not absorbed.

and at an even greater rate. At the same time, however, grain growth will take place among the small grains, so that presently the large grains will no longer encounter the very small, easily absorbed grains, but will meet grains of more nearly their own

size, which have developed in the fine-grained regions. Grain growth may then cease, leaving the metal as shown in Fig. 63.

Conditions commonly found in metals differ only in degree from the extreme case just described. There are always some differences in growth force from point to point in the metal, and corresponding differences in the temperature at which grain growth will begin. If the metal is heated at a temperature sufficiently high to cause grain growth at some points, but not high enough to cause general growth all through the metal, conditions are favorable for the development of large grains. However, the points at which early growth begins may be so close together that the grains developed are no larger than those normal to the temperature used. On the other hand, if the centers of growth are far apart, abnormal grain growth results. It is this preferential growth of certain grains to abnormally large size which is termed "germination."

All kinds of plastic deformation unavoidably produce local, if not general, strain gradients. The strain or fragmentation varies from one region of the metal to another, from grain to grain, and in different portions of the same grain. The greater the strain the lower is the temperature at which grain growth will take place on heating. Hence, in a uniformly cold-worked metal the points of greatest strain are the ones which act as the centers of germination. The grain size produced will be larger as these centers are farther apart. This condition is favored by *slight* deformation. Severe deformation tends to make the strain or fragmentation more nearly uniform throughout the metal, and brings the points of equal strain closer together. Abnormal grain growth is therefore most commonly obtained after mild deformation.

Sauveur found that a piece of mild steel stressed in tension to 40,000 lb. per square inch developed unusually large grains on annealing at 650° C. If stressed to only 38,000 lb. per square inch, this grain growth did not take place. This simply means that a stress of 40,000 lb. per square inch developed at a *few* points strain great enough to cause growth at 650° C. in the time allowed. At 38,000 lb. per square inch the greatest strain produced was not sufficient to cause grain growth under these conditions. If a slightly higher temperature or a considerably longer time had been used, germination would have resulted in this case too. On increasing the stress to 42,000 lb. per square

inch and maintaining the same conditions of annealing, grain growth occurred, but the grain size produced was comparatively fine. The centers of germination were in this case close together.

When a metal is heated rapidly through the germinative temperature, the preferential growth of a few grains is prevented because at the higher temperatures a very large number of grains are capable of growth. It might be said that they fail to attain abnormally large size because the competition is more keen.

The method of Ruder for producing excessively large grains in silicon steel and of Schaller for producing coarse-grained tungsten wire is based on a very simple type of germination. The grain size of the starting material is sufficiently fine so that marked grain growth of the normal variety will occur at and above a suitable temperature, which will be called T . The metal is then heated so that one region is above this temperature T , but the major portion is below this temperature. In the region heated above T , grain growth will occur and there will be produced grains considerably larger than those in the colder or "inert" region, where no grain growth is taking place. (It appears that a certain amount of mechanical obstruction helps to prevent the coalescence of the small grains.) At the junction between the large grains of the growth region and the small grains of the inert region, conditions are ideal for the continued growth of the large grains at the expense of the smaller, exactly as in the hypothetical case described above in Fig. 61. The metal is now moved through the heated zone at a rate less than that at which the germinant grains can absorb the inert ones. Advancing the line of the growth temperature T at a faster rate would defeat the production of coarse grains, just as does rapid heating through the germinative temperature.

The samples from which the "Germinative" curve in Fig. 54 was obtained illustrate the effect of a temperature gradient nicely. When heated to an average temperature of $2,600^{\circ}\text{C}$. by electric current and maintained for about 10 min., a few large grains formed about midway between the axis and surface of the rod. The hotter portion, near the axis, was composed of larger grains than the cooler surface portions. This shows that growth had taken place near the axis, but not at the surface. The few large grains were located at the boundary between the axial portion, which may be called *growth range* and the surface



FIG. 64.—Germinant grains in position to absorb small grains in tungsten.
× 25.



FIG. 65.—Enlarged portion of Fig. 64. × 100.

portion, or *inert range*. The inert grains were only inert in so far as concerns absorption by grains of their own size. Before heating, the grain size or particle size was uniform from axis to surface of the briquet. Of course, there were local differences, but no general differences. A mean temperature of $2,600^{\circ}\text{C}$. was proper to cause growth in the hotter axial portion, but not near the surface. There must then be a boundary between the growth and inert regions. The inert region is inert because of lack of grain size contrast. Some grains in the growth range at the boundary between growth and inert regions increase sufficiently in size to absorb the inert grains and hence greatly increase in size. These grains are the "germinant" grains. The grains well within the growth range are small compared to the germinant grains, because of lack of grain size contrast. When the germinant grains reach a size considerably larger than the grains in the growth region, the latter are absorbed. The germinant grains then grow toward the surface and toward the axis, eventually producing a very coarse-grained structure, as indicated in Figs. 64 and 65. The various grain sizes produced by varying the rate of heating through the germinative temperature range in these samples are in exact accord with the hypothetical case cited in Figs. 61 to 63. If the temperature is lowered a little below $2,600^{\circ}\text{C}$., the germinant grains form nearer the axis, and with mean temperature a little above $2,600^{\circ}\text{C}$., they form nearer the surface.

In the germinative conditions due to obstruction (Fig. 55) it was observed that the germinant grains formed first near the surface of the briquet in the 2.5 per cent thoria sample, about half way between the axis and surface in the 3 per cent thoria sample, and near the axis in the 4 per cent thoria sample. The boundary between growth and inert ranges (germinative temperature) was thus at higher temperatures for the greater amounts of obstruction.

It is evident that the presence of a strain gradient in a piece of metal may lead to germination even on uniform heating. When the strain varies continuously as in Chappell's tapered bar (Fig. 53), there is some region where the degree of strain is just right to cause germination at the temperature used. After germination has taken place, there is a condition similar to that described above—that is, a region of very large grains bordering on the unrecrystallized region of very small grain fragments.

Grain growth will then proceed to some extent into this region, but will come to a halt when the strain decreases to a certain value. It should be especially noted that, when there is a strain gradient, germination may be obtained at any temperature within a rather wide range. When the strain is substantially uniform, there is only one temperature, or a narrow range of temperature, at which coarsening will take place. For this reason the chances of obtaining coarse-grained structures in industrial annealing or under high-temperature service conditions is much greater when the strain is not uniform.

The important effect of the obstruction factor on germination has been pointed out. It has been seen how germination in steel is most marked for a certain range of carbon content (0.04 to 0.12 per cent). In tungsten heated under certain conditions the addition of a small amount of thoria refines the grain. More thoria causes germination, with the production of relatively enormous grains. Still more thoria inhibits growth to such an extent that no abnormally large grains are produced below the melting point. The same cycle has been shown to obtain on the solidification of a certain aluminum alloy under constant cooling conditions. The first addition of obstructing material refined the grain. A further addition caused marked coarsening, and a still further amount again refined the grain. It is not to be inferred from these examples that the progressive addition of obstruction always results in germination. Germination is, in fact, the exception rather than the rule. When germinative conditions *are* produced, however, the rule is that the progressive addition of obstructing material causes, first, refinement, then coarsening, then refinement. Often the first stage is not marked—that is, the first addition of obstruction may not produce a grain size noticeably smaller than in the pure metal. The germinative stage is most marked, and the return to normal grain size on the addition of more obstruction is, of course, equally apparent.

On analyzing the conditions under which these cases of germination occurred, it is found that in Sauveur's uniformly stressed bars the coarsening resulted from local strain gradients, while in the tungsten briquets temperature gradients are responsible. In the solidifying aluminum alloy, temperature and concentration gradients exist and there is unavoidably at any one time a difference in the size of the newly formed solid grains which corresponds to a strain gradient. These three cases therefore

involve the principal factors which at various times cause germination. The fact that the effect of progressive additions of obstructing matter follows the same law in all cases indicates a similarity of mechanism.

Differential Growth Velocity.—Any case of germination in the solid state depends upon the existence at some stage of a marked grain size contrast, as pictured in Fig. 61 or as described in connection with the Schaller process. This condition is always present when there are strain gradients, either general or local, since strain is equivalent to grain fragmentation. At other times, however, the grain size contrast is not present in the original material, but is developed during the heating as the first stage of the germinative process. This is true of the Schaller process and, in general, of cases where germination is brought about by temperature gradients. Once this condition of grain size contrast obtains, it is necessary, in order for germination to proceed, that the metal be held at a temperature where the rate of growth of the larger grains is very great as compared with that of the smaller grains among themselves. The condition for germination may be stated as follows: *The existence of marked grain size contrast in a metal at a temperature which permits absorption of the small grains by the larger, but not growth among the smaller grains.*

Germination thus depends upon a sharp difference in the rate of grain growth from point to point in a metal. It seems probable that the important effect of mechanical obstruction on germination is brought about through the establishment of such differences in growth velocity. It may well be supposed that a given obstructing material, present in given quantity and mode of distribution, exerts its maximum obstructing effect on grain growth with respect to grains of a certain size. If such is the case, then the presence of obstruction may accentuate the differences in growth velocity already present because of varying grain size, and thereby increase the probability of germination.

Suppose an obstructing material to be present in a metal to an extent of 1 per cent by volume, and to be uniformly distributed in the form of spheres having an average diameter of 0.0001 in. Assuming, for the purpose of calculation, a simple cubic distribution, the shortest distance between particles is about 0.0004 in., or about four times the diameter of the particles. Now suppose the grains of the metal to be smaller in diameter than the particles.

It is obvious that the particles can have no important effect on the growth of such small grains, since so few of the grain boundaries come in contact with them. If the grains are about the same size, or slightly larger, than the obstructing particles, the interference with grain growth will also be small in the present case, because of the distance apart of the particles. When the average grain diameter is of the same order of magnitude as the distance between obstructing particles, a rather marked hindrance to growth may be expected. Grains of very much larger size should suffer less interference because the relative distortion of their boundaries by the obstructing particles during growth by boundary migration would be less. It is therefore reasonable to assume that the obstruction to grain growth due to discrete particles scattered through a metal is greatest for a certain range of average grain diameter which is approximately equal to the average distance between particles.

According to this hypothesis, the first addition of an obstructing material to a metal would restrict the growth chiefly of the larger grains. Since these grains are already endowed with superior power of growth, the presence of such an amount of obstruction would *decrease* the difference in growth velocity between the larger and the smaller grains. The growth of grains of all sizes is opposed to some extent, so that the general effect may well be one of grain refinement. Upon further addition of obstruction, a point will be reached where the maximum retarding effect is on those smaller grains upon which the larger germinant grains feed. Conditions are then most favorable for germination. Still further additions of obstructing material may so increase the general resistance to growth that all grains are kept relatively small.

Formation of Nuclei.—It has been stated above that, in the opinion of the present authors, no new crystalline nuclei are formed during recrystallization. There is no evidence that such nuclei are formed except on the appearance of a new crystalline phase, which occurs in the following cases: (1) solidification from the molten state, (2) allotropic transformation, (3) separation from solid solution, (4) electrodeposition. The first two of these are most important in connection with grain growth.

Growth of the nuclei proceeds by two distinct processes. First, they feed upon the unstable disappearing phase—that is, the molten metal or the unstable allotrope (as the case may be).

Second, if the temperature and other conditions are suitable, the larger of the new crystalline units grow at the expense of the smaller by the processes of ordinary grain growth. The resulting grain size therefore depends both upon the conditions affecting nucleus formation and upon the conditions affecting grain growth in the new phase.

Both of these factors are illustrated in the allotropic transformation of iron at A_3 (about 900°C.). Suppose a piece of iron at a temperature above A_3 to be cooled very slowly from one end, so that there is a continuous temperature gradient toward the hotter end. As the cooler end passes A_3 , grains of the new crystalline phase appear and grow at the expense of the adjacent disappearing high-temperature allotrope. If a sufficiently sharp temperature gradient can be maintained and advanced at a rate lower than the velocity of grain growth, the grains first formed might sweep the entire piece of metal, as in the Schaller process. Slow cooling through A_3 , accompanied by temperature gradients, is, therefore, conducive to the formation of coarse-grained ferrite.

Slow cooling alone produces distinctly larger grains than rapid cooling. This is attributable to grain growth in the ferrite just after cooling through the A_3 temperature. The rigidity of the metal at this temperature is so great that it is possible to completely form the new phase with a grain size much smaller than the equilibrium grain size. Any exposure to temperatures immediately below A_3 therefore results in normal grain growth.

Other conditions being the same, the grain size of the new allotrope formed on heating or cooling through A_3 is roughly proportional to the grain size of the modification from which it was formed. This principle, which has been called "grain size inheritance," is believed to depend on the fact that the nuclei of the new phase form most readily in the old grain boundaries.¹

The fact that grain growth is seldom if ever observed on reheating single-phase cast metals is perhaps responsible for a rather general belief that there is no growth at the expense of solid grains during the solidification of metals. This belief leads to the conclusion that all of the crystalline nuclei formed persist, so that the number of grains in the solid metal is equal to the total number of nuclei formed during solidification. The grain

¹ JEFFRIES, ZAY, "Grain Size Inheritance in Iron and Carbon Steel," *Trans. Am. Inst. Mining Eng.*, vol. 58, pp. 669-695, 1918.

size of a cast metal is then held to be a direct consequence of the laws of nucleus formation. This theory of the solidification of metals has been particularly developed by Tammann.¹

The present authors have indicated above their opinion that normal grain growth, involving the absorption of solid grains, occurs during and perhaps shortly after solidification. On this basis, the number of grains left on cooling is very much less than the number of nuclei formed. There is considerable evidence that actual solidification is preceded by the formation in the liquid of groups of atoms which are essentially crystalline nuclei, and yet obviously some of these groups are absorbed by others during solidification.

Germination in a solidifying alloy may be explained in very much the same way as germination in a solid metal. In the case cited, the first addition of obstructing material caused general interference with growth, but with a maximum effect on the larger potentially germinant grains. A further addition produced germinant conditions by exerting a maximum obstructing effect on the smaller grains, thereby preventing them from coalescing into large grains of greater resistance to absorption. Finally, the obstruction became so great that no grains could attain abnormally large size.

The Distortion Theory of Grain Growth.—Within recent years there has been developed, largely by Czochochalski,² an interesting theory that grain growth is caused by varying distortion of the crystal lattice. It is known that when a metal is cold worked, internal stresses are left which must necessarily involve elastic distortion of the grains or grain fragments. It is also quite certain that the amount of relative distortion varies from grain to grain. The grains which are distorted the least are most stable and are, from the thermodynamic point of view, in a position to grow at the expense of the more severely distorted crystalline material. The distortion theory postulates that when such growth takes place the atoms added to a grain arrange themselves in a lattice having exactly the same degree of distortion as that of the growing grain. Grain growth then involves a progressive decrease in the elastic energy of the metal due to lattice distortion. At any given temperature a state of metastable equilibrium is reached.

¹ Text Book of Metallography (in German), 1914.

² *Intern. Z. Metall.*, vol. 6, pp. 289-296, 1914; also MASING, *Z. Metallkunde*, vol. 12, p. 457, 1920.

On heating to higher temperatures, the decreased inertia enables more growth to take place, always with a differential distortion as the cause.

This theory accounts very nicely for the absence of growth in unstrained castings, and fits in well with many of the grain growth phenomena. It depends, however, upon an assumption (which appears to the present authors so improbable as to require quite definite proof) that lattice distortion, and hence internal stress, exists in metals which have been fully annealed. The effect of heat upon internal stresses has been fully investigated in connection with the season cracking of brass, and it has been found that these stresses are reduced to a vanishing point by heating *below* the temperature of recrystallization. It does not therefore seem likely that at temperatures several hundred degrees higher any appreciable distortion can exist. The surface energy due to small grains is present at all temperatures, and can be reduced only by grain growth. On the other hand, cast metals can be obtained in a condition of internal stress nearly equal to the elastic limit and involving practically the maximum possible lattice distortion in some of the grains. This distortion can be removed on heating without causing any grain growth. Such considerations lead to the conclusion that surface energy is the principal cause of grain growth.

General Propositions.—1. Crystalline nuclei are formed only on the appearance of a new crystalline phase.

2. Crystalline nuclei may grow by the absorption not only of the disappearing phase but also of each other, so that the final number of grains may be less than the total number of nuclei formed.

3. Grain growth results from the tendency of metals to assume the form of greatest possible physical stability.

4. The principal conditions conducive to grain growth are small grain size and grain size contrast.

5. Grain growth is opposed by mechanical obstruction and by inertia due to low temperature.

6. A condition of metastability as regards grain growth must be recognized, in which, while the metal is not in the most stable form, the forces tending to cause grain growth are insufficient to overcome the opposition to growth. As the temperature rises, this condition of apparent equilibrium approaches that of maximum stability.

7. Recrystallization is essentially grain growth on a submicroscopic scale.

8. Germination consists in the preferential growth of certain grains favored by their large size. The necessary condition is the existence of grain size contrast and suitable temperature such that the larger grains can grow at a considerably more rapid rate than the smaller grains.

9. There is a critical amount of mechanical obstruction which favors the establishment of this necessary difference in growth velocity, and hence germination.

CHAPTER VI

MÉCHANICAL PROPERTIES OF METALS

Broadly speaking, the mechanical properties of metals are those properties which describe the behavior of metals in the mechanical arts. The conditions to which metals are subjected, both in service and in the fabricating processes which precede service, are of unending variety, so the engineer is confronted with the problem of determining the suitability of metals for the various conditions of fabrication and of service. It is to meet this problem that the science of mechanical testing has been developed.

The most certain evidence of the behavior of a metal under a given set of working conditions consists in the accumulated results of many trials under those conditions. Actual working conditions are often very complex, however, and the accumulation of such evidence is a long, slow, and costly process. It is, therefore, desirable to analyze the complex conditions into a relatively small number of more simple elements. The common tests of metals, such as the tensile test, are designed to determine these more elementary properties.

Complexity of "Simple" Properties.—A mechanical test is merely a mechanical operation in which the variables are controlled and the results quantitatively measured. The smaller the number of independent variables the more easily are they controlled and hence the greater the accuracy of the test and the more fundamental the nature of the property disclosed. Considering the "simple" mechanical properties of metals in this light, it is found that they are quite complex in comparison with the properties regarded as fundamental physical constants. The melting point, for example, of a metallic element is sufficiently fixed for practical purposes to be regarded as absolute. Pressure and grain size exert a slight but negligible influence. The tensile strength, on the other hand, cannot be stated with satisfactory accuracy, even for a pure metal, without defining the temperature, structure of the metal, form and size of test piece, and rate of loading.

There is, therefore, a need for still further simplification in testing—that is, for further analysis of the common mechanical properties and the defining of properties of a more fundamental nature. Such an analysis must be made with the assistance of all the knowledge afforded by metallography of the structure of metals, and the effects of deformation and temperature on structure. Attempts have been made and are unfortunately still being made to solve these problems by pure mathematics.

The analytical method is, of course, limited. Even if it were possible to define all of the fundamental constants upon which the mechanical properties of metals depend, and to determine them, the synthesis of these elements into results of direct utility would undoubtedly present such difficulties that in many cases the empirical method of attack would be more easy and more certain. Such a knowledge of fundamentals would be invaluable, however, in classifying empirical information and in pointing the way to new knowledge.

It is almost needless to say that a fundamental study of the properties of metals and alloys should begin with the pure metals. There has, nevertheless, been some tendency to give the properties of the pure metals less attention than they deserve, perhaps because of failure to recognize their true complexity. While it is true that metals are most widely used in alloyed form, it is also true that a fundamental understanding of the properties of the alloys requires an understanding of the properties of the pure metals upon which they are based.

Classification of Properties.—All of the mechanical tests consist in observing quantitatively the behavior of metals under stress, the various tests being differentiated by the type of specimen and the manner and rate of application of stress. According to the rate of application of load, tests are often divided into two classes, called “static” and “dynamic.” The so-called static tests include the ordinary tension, compression, torsion, and transverse tests, as well as the Brinell hardness test. The Shore scleroscope test for hardness would also probably be classified as a static test. The dynamic tests include the various types of alternating stress or fatigue tests and the single and repeated blow impact tests. (Another division is sometimes made into static tests, repeated stress tests, and impact tests.)

The effects of stress are deformation and rupture. The mechanical properties of metals may be classified in a general way in

three groups, describing (1) *resistance* to deformation and rupture, (2) *capacity* for deformation without rupture, and (3) *work* of deformation or rupture.

In the first group, which may be designated by the general term *hardness*, are included the elastic limit, elastic modulus, tensile strength, transverse strength, shearing strength, endurance limit under repeated stresses, Brinell hardness, scleroscope hardness, etc.

The second group may be covered by the term *plasticity*, and includes the elongation and reduction of area in the tensile test, the relative compression without rupture in the compression test, the angle of twist in the torsion test, the deflection at failure in the transverse test, angle of bend in the bend test, as well as the general properties denoted by the terms "ductility" and "malleability."

The work of deformation and rupture is the product of the resistance to deformation by the amount of deformation, and can be calculated from the complete data of any test in which both load and deformation are observed continuously or at close intervals. It is represented by the area under the stress-strain curve. The only common test in which the work is measured directly is the single-blow impact test.

In a test specimen subjected to simple stress, as tension or compression, the energy of deformation is applied uniformly to all of the metal under test, as long as the deformation is elastic. The energy is stored as elastic energy, recoverable on removal of the load, and is called *resilience*. The work expended in deforming unit volume of a material to its elastic limit is the *modulus of resilience*.

When the elastic limit is exceeded, plastic deformation may take place in a fairly uniform manner, as when a tensile specimen draws out evenly without necking. The work of permanent deformation may then be calculated per unit volume of the metal. When the deformation ceases to be uniform, as when necking occurs, it is no longer possible to refer the energy to a definite volume of metal. Supposing the stress-strain diagrams of two tensile test bars to show the same total work of rupture, the maximum energy absorbed per unit volume of metal will be in the bar having the greater reduction of area.

Cause of Hardness and Strength.—Metals owe their resistance to deformation to the forces between the atoms. These forces

are both attractive and repulsive. The repulsive forces are manifested by the resistance of metals to hydrostatic pressure, by which the atoms are forced closer together in all directions. Under ordinary compression loading, the atoms are forced together in the direction of the compression, but apart in the direction of the secondary tensile stresses. Under direct tension the distances between atoms are increased in the direction of the load and decreased in the direction—at right angles—of the secondary compressive stresses. There is no condition of loading corresponding to a negative hydrostatic pressure, under which the interatomic distances would be increased in all directions.

Any permanent deformation of a metal involves changes in the relative positions of some of the atoms, and, therefore, the breaking, temporarily at least, of some interatomic "bonds." The rupture of any material, whether with or without permanent deformation, also involves the breaking of interatomic bonds. The greatest possible resistance that a material can offer to deformation or rupture is the summation of all the interatomic bonds on a plane through the specimen normal to the stress, a summation which may for convenience be termed the *absolute cohesion* of the material. Actually, such a summation of forces is never realized, because rupture always takes place by degrees, and the breaking of atomic bonds is not simultaneous. The tensile strength of a material merely represents the maximum number of atomic bonds that come into play simultaneously during the test.

Absolute cohesions of metals are far in excess of the values obtained for tensile strength. A qualitative illustration of this fact may be found in a consideration of some properties of pure iron. The tensile strength, after hot rolling, is about 40,000 lb. per square inch, a value representing, as usual, the maximum load divided by original cross-section. If the actual reduced area of the test piece is measured throughout the progress of the test and the stress computed on this basis, a value will be found for the maximum stress which is much higher than the tensile strength. The maximum stress will then be about 80,000 lb. per square inch. Severely cold-worked iron may show a tensile strength of 150,000 lb. per square inch. The maximum actual stress is again somewhat higher (165,000), but not in so large a ratio as in the case of the hot-rolled iron. Even in the cold-worked iron, rupture

still takes place by degrees—that is, by a kind of tearing action—so that the highest of these figures still does not represent the inherent absolute cohesion.

Some very interesting tests of glass have been reported by Griffith.¹ In ordinary fibers of 0.040 in. diameter the material had a tensile strength of about 25,000 lb. per square inch. The tensile strength was found to increase as the diameter of the fibers decreased, and in very fine fibers, carefully prepared, surprisingly high values were obtained. The maximum strength recorded was 492,000 lb. per square inch at a diameter of 0.00012 in. Plotting the reciprocal of the tensile strength against the diameter of the fiber and extrapolating to zero diameter, Griffith found a value of 1,600,000 lb. per square inch, representing the theoretical absolute cohesion of the glass.

Calculations based on the energy required to separate the atoms of metals by vaporization give values up to about 5,000,000 lb. per square inch for the “intrinsic pressure,” a quantity which is theoretically of the same order of magnitude as the absolute cohesion.

The accuracy of Griffith's extrapolation and of values for cohesion derived from the heat of vaporization may be questioned. The actual numerical values reached are of little significance. The important thing is that metals possess very great inherent cohesion, greater probably than is ever realized in tensile tests of the pure metals or their strongest alloys. Looked at from this point of view, the problem of the hardening and strengthening of metals by various means becomes more simple. Instead of inquiring why metals are so strong, it may better be asked why metals are so weak.

Nature of Plasticity.—Permanent deformation of any material involves displacements within the material, during which the cohesion is overcome between the parts undergoing relative displacement. The property of plasticity depends upon the ability of such displaced parts to reestablish cohesion in their new positions. This ability is a conspicuous characteristic of liquids, and the plasticity of many materials depends on the possession of a structure like that of liquids, or on the presence of some liquid, to preserve continuity during deformation. Glass is a typical example of undercooled liquid which at certain

¹ GRIFFITH, A. A., “The Phenomena of Rupture and Flow in Solids,” *Phil. Trans.*, Series A, vol. 221, pp. 163–198.

temperatures is distinctly plastic. Even after cooling to temperatures of great rigidity, its structure is still that of a liquid, in the random arrangement of molecules. Clay, on the other hand, owes its plasticity to the presence of a continuous matrix of water which holds together the fine particles of non-plastic solid matter.

According to the amorphous metal hypothesis of Beilby, metals preserve their continuity during plastic deformation by the generation of fluid amorphous films on the surfaces of slip. On this basis, the plasticity of crystalline materials depends on their ability to generate such amorphous films. It is quite conceivable, however, that crystalline fragments might adhere to each other without the intervention of a layer of undercooled liquid or vitreous amorphous material.

Complexity of structure is opposed to plasticity. The molecules of a liquid establish cohesion bonds with each other easily, without the necessity of any particular arrangement. Hence, two bodies of a given liquid unite with each other on contact. When contact is brought about between two solids whose rigidity depends upon a highly organized structure, the establishment of cohesion is not so easy. When a piece of wood, for example, is broken in two, it is practically impossible to replace the parts either in their original positions or in any other positions in which cohesion is reestablished. In metals the structure, though crystalline, is relatively very simple. It is easily imagined that the fragments of a metallic crystal broken along a crystallographic plane might be brought into contact on this plane in registry so that the original space lattice, and hence cohesion, might be reestablished. Probably plastic deformation of metals involves both this type of junction and junction by more or less disorganized or amorphous metal. The monatomic condition of aggregation of the metals and their simplicity of crystalline structure favor both mechanisms.

Common Properties of Commercial Iron.—In Table VI are given the common mechanical properties of a very pure grade of iron, in the annealed condition after working. The tests were all made at ordinary temperatures and under usual conditions. Besides giving useful information about this most important metal, these figures will serve to illustrate a brief discussion of some of the mechanical properties.

The elastic and proportional limits are practically identical. Difference in the values given reflects chiefly the difficulty of an

accurate determination—the actual results obtained depend on the sensitivity of the measurements of extension. When metals are tested at temperatures well below that of recrystallization, the passing of the elastic limit represents the beginning of plastic deformation by transcrystalline slip. At temperatures near or above the recrystallization temperature, intergranular flow may take place and mark the elastic limit; the stress required varies greatly with the time of application.

The yield point is well marked in iron and mild steel, representing a considerable extension at nearly constant stress. During

TABLE VI.—PROPERTIES OF ANNEALED ARMCO IRON

Property	Value	Remarks
Elastic limit in tension, pounds per square inch	14,400	
Proportional limit in tension, pounds per square inch	16,100	
Yield tension, pounds per square inch	19,000	
Ultimate tensile, pounds per square inch	42,400	½-in. diameter specimen
Ultimate tensile, * pounds per square inch	48,200	0.025-in. diameter specimen
Per cent elongation in 2 in	48.3	½-in. diameter specimen
Per cent elongation in 2 in.*	23.7	0.025-in. diameter specimen
Per cent reduction in area	76.2	½-in. diameter specimen
Per cent reduction in area*	76.0	0.025-in. diameter specimen
Elastic limit in compression, pounds per square inch	19,400	
Proportional limit in compression, pounds per square inch	19,200	
Yield point in compression, pounds per square inch	20,600	
Ultimate in compression, pounds per square inch	31,200	
Elastic limit in torsion, pounds per square inch	12,400	
Proportional limit in torsion, pounds per square inch	12,500	
Yield point in torsion, pounds per square inch	13,600	
Modulus of elasticity in torsion, pounds per square inch	11,770,000	
Young's modulus in tension and compression,* pounds per square inch	30,000,000	
Endurance limit, Farmer rotating beam, pounds per square inch	26,000	
Endurance limit, Olsen-Foster reversed torsion, pounds per square inch	12,500	
Brinell hardness number*	75	
Shore scleroscope hardness	18	
Energy of rupture on impact, foot-pounds	19.3	Specimen 0.391 in square, notched to ½ depth, bottom of notch 0.04 in. radius.

* With the exception of the properties marked with asterisk, the results given in this table were reported by H. F. Moore, Eng. Expt. Sta., Univ. of Ill.

this stage, movement on slip planes is general throughout the specimen; the effect is visible on the machined surface of a test bar, which becomes dull. In non-ferrous metals the yield point is not nearly so well marked and can be defined only as the stress at which some arbitrarily selected extension occurs.

Up to the elastic limit, the metal is not permanently altered by the application of the test load. Beyond this point, however, the deformation incident to the test alters the structure and properties of the metal. Elongation, reduction of area, and tensile strength therefore depend not only on the original condition of the metal but also upon the effect of the testing operation itself. The mechanism and effects of plastic deformation must be considered in interpreting the results of tests in which the metal is plastically deformed.

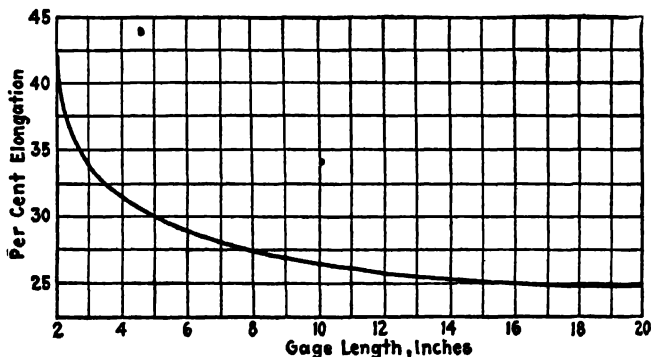


FIG. 66.—Effect of gage length on elongation of soft steel. Test piece 0.088 in. in diameter.

General and Localized Elongation.—Most of the ductile metals draw down at the point of fracture, so that the relative elongation at this point is greater than the general relative elongation along the bar. Total elongation as measured is, therefore, made up of two parts, one a general elongation approximately uniform along the bar and the other a variable local stretch where the bar necks down. The maximum local stretch can be calculated from the reduction of area on the assumption that the volume of the metal remains constant (which is practically true). When the reduction of area is high, the per cent elongation on the constricted portion of the bar may be several times the per cent general elongation. Hence, on bars of the same cross-section, the per cent elongation, measured so as to include the fracture, is greater

the shorter the gage length (see Fig. 66). If the gage length remains constant but the test bars differ in cross-section, then the per cent elongation is greater on the larger bar, as illustrated by the values given in Table VI. The gage length is 2 in. in each case. On the $\frac{1}{2}$ -in. test bar the per cent elongation was 48.3 made up largely of the local stretch at the fracture. Wire of 0.025 in. diameter showed elongation of 23.7 per cent, representing almost solely the general elongation—since the contribution of the small local stretch is in this case negligible.

Reduction of area in tension is characteristic both of the metal and the conditions of test. General elongation is to a similar extent characteristic of the metal; elongation as commonly measured, however, includes a factor which is proportional to reduction of area. Reduction of area and general elongation are not affected in the same way by changes in temperature and other variables. Since the measured elongation includes both factors, it will be found that the effect of temperature and other conditions depends largely on the ratio of gage length to cross-section. The relative elongation found by the tensile test is the most common criterion of ductility, the general elongation being probably a better indication than the total elongation measured over a short gage length.

Ductility and Malleability.—Ductility is capacity for being drawn out, or plastically deformed, by direct tensile load without rupture. It is a property which requires both plasticity and tensile strength, and does not, therefore, necessarily reach a maximum value when plasticity is at a maximum—most metals have the greatest plasticity above the recrystallization temperature, but greatest ductility below the recrystallization temperature; they have not sufficient tensile strength above the recrystallization temperature to sustain the loads necessary to draw them out. Malleability is capacity for plastic deformation without rupture by hammering. It does not require as much resistance to tension as does ductility, since the metal is not subjected to the entire deforming load in direct tension. Secondary tensile stresses are developed, however, of greater or less magnitude, depending on such factors as the manner of hammering and shape of dies. Some strength is therefore required, in the absence of which the metal is said to be “tender.” The process of drawing out by swaging in confined dies is less exacting on the strength of the metal than are most forms of hammering, and can some-

times be carried out when successful working by hammering is not possible.

There are no fixed standards of plasticity, ductility, and malleability. In fact, these properties are so loosely defined that they cannot be expressed accurately even in relative terms. While the term "plasticity" refers chiefly to *capacity* for deformation, it also carries some implication of *ease* of deformation. Consider iron, for example, at the temperatures 1,000 and 1,100° C. At either temperature it can be plastically deformed to an almost unlimited extent. It is softer at the higher temperature, however, and would commonly be considered more plastic. Since it can be deformed more easily by hammering or rolling at the higher temperature, it would also be generally considered more malleable. Ductility refers more definitely to capacity for deformation by drawing, but there are various ways of estimating such capacity. Some of the older tables, in which the metals are arranged in the order of ductility, are based on the fineness of the wire which can be, or rather has been, drawn, just as the tables of malleability are based largely on the thinness of the sheet or foil that can be beaten. Another criterion is the total reduction in section, or extension in length, possible by drawing without intermediate annealing; on this basis copper is much more ductile than iron at room temperature. Relative ductility is also sometimes measured by the maximum reduction possible in the first die or the first few dies. In this respect iron is more ductile than copper.

It will be noted in Table VI that the tensile strength of the iron wire is about 14 per cent higher than that of the $\frac{1}{2}$ -in. test bar. Presumably, the two materials are similar as to structure, and the difference in strength is in accordance with the general observation that tensile strength increases as the diameter of the material decreases. This has been recognized in standard specifications for wire.

It is remarkable that this material showed an endurance limit under repeated stress about 60 per cent higher than its elastic limit in tension. Although there is no general law connecting endurance limit with the static properties, the endurance limit is usually less than the elastic limit in tension. It may be remarked in passing that the endurance stress of 26,000 lb. per square inch given in the table was calculated from the formula for a transversely loaded beam, which depends upon the assump-

tion of perfect elasticity, yet the calculated stress is well above the known initial elastic limit of the metal.

Rate of Loading.—Time plays an important part in the behavior of metals under stress. Thurston¹ divided metals and alloys into two classes, according to whether or not they exhibited flow under prolonged application of stress. At ordinary temperatures, iron will sustain indefinitely any load which it will sustain for a short time. Many of the non-ferrous metals, however, especially the softer metals, like lead, tin, and zinc, yield gradually under constant load; in the course of years, lead roofing will creep under its own weight.

Variations in the rate of applying load in the ordinary tensile test have a marked effect on both tensile strength and elongation of soft metals, which are, as a rule, increased by increasing the rate of loading. Ordinary variations in the rate of testing have practically no effect on the tensile properties of iron and steel. Under extremely rapid loading the elongation may be increased. Some tests have been reported by Maitland² on a steel which had a tensile strength of 58,000 lb. per square inch with an elongation of 27 per cent in 2 in. when broken in the usual manner. A specimen was screwed in blocks arranged so as to fall vertically in a slide for a certain distance, when the top block was arrested by stops and the specimen was broken by the momentum of the lower block. Broken in this manner the elongation was 47 per cent. The rate of loading was still further increased by driving the ends of the test bar apart by exploding gunpowder or gun-cotton. Under these circumstances the elongation was up to 62 per cent. Such increases by rapid loading are not always obtained.

Instead of causing failure at a low stress, extremely slow loading of iron causes a considerable increase in tensile strength. Wires broken after a gradual application of load during about 2 months gave a tensile strength about 25 per cent higher than that obtained in a quick test. This behavior, which is peculiar to iron in its magnitude, will be discussed later and correlated with other properties.

Time plays an unimportant rôle in causing fatigue, especially in iron and steel. Thus the metal can be subjected without

¹ THURSTON'S "Materials of Engineering," Part 3, "Alloys, Brasses and Bronzes," p. 489, John Wiley & Sons, Inc.

² "The Treatment of Gun Steel," *Proc. Inst. Civil Eng.*, vol. 89, p. 120.

failure to a static load, much greater than its endurance limit under repeated stresses for a period of time greater than that required in the fatigue test. It is the reversal of deformation rather than the prolonged application of load that does the damage.

There has long been a rather general belief that metals, particularly iron and steel, break more easily under suddenly applied load—*i.e.*, shock or impact—than under slowly applied load. Impact tests have been made on rails and axles as a matter of routine inspection, to determine their susceptibility to easy fracture by shock. Several types of impact testing machine have been developed; the most common one breaks a notched bar by a single blow and measures the energy of rupture. It has been shown that for many kinds of steel the energy absorbed is practically the same whether the bar is broken in the impact machine or by slow bending. In other words, the test is merely a bend test of a notched bar. Some steels, however, appear to break much more easily by rapid than by slow bending.

Temperature Scale.—The recrystallization temperature constitutes a point of division in the temperature scale of a metal—at higher temperatures the metal is “hot” and at lower temperatures “cold.” Deformation at 250° C. is hot working for lead or zinc but cold working for iron or nickel. When the various ductile metals are compared at a fixed temperature, such as the ordinary atmospheric temperature, they are found to be widely different in mechanical properties, but if the comparison is made at temperatures similarly related to the respective recrystallization temperatures, the metals are found to be not so unlike.

Below the temperature of recrystallization the structure of a metal is relatively permanent. Any change produced by deformation prior to a mechanical test or by the deformation incident to the test itself is cumulative. Above the recrystallization temperature, on the contrary, the internal structure is constantly subject to grain growth which largely wipes out the effects of deformation. Material at grain boundaries also possesses a much greater capacity for viscous flow under stress than at lower temperatures. The phenomena encountered in the two temperature ranges therefore fall naturally into different classes.

There is another fairly marked but not very definite point in the temperature scale of a metal. It is the temperature at which the metal becomes brittle on cooling. Iron in the annealed con-

dition is ductile at room temperature but brittle in liquid air (-185°C.) unless very fine-grained. Equiaxed tungsten wire is ductile at 200°C. but brittle at room temperature. Annealed copper, however, is ductile at the lowest temperatures at which it has been tested. In general, the temperature at which brittleness appears on cooling is highly dependent on the structure of the metal. This brittleness is often accompanied by low or erratic strength, due to the easy development of high local stresses by eccentric loading. It follows that values for strength are likely to be most dependable when the temperature of test is such that there is appreciable ductility.

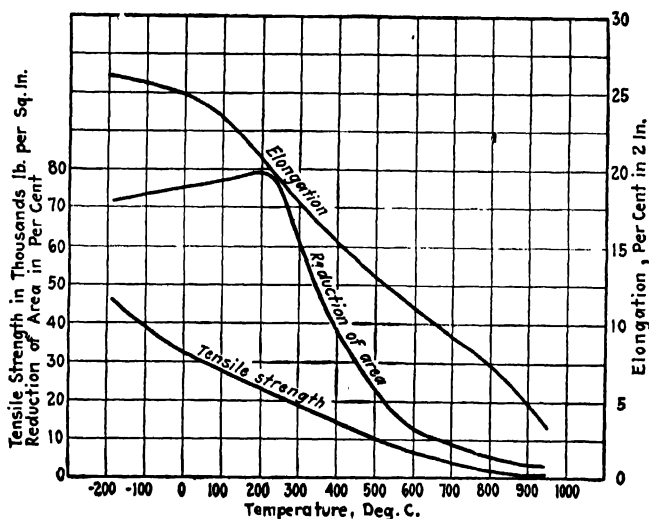


FIG. 67.—Effect of temperature on tensile properties of annealed copper wire.

The temperature scale of a solid metal can thus be roughly divided into three regions: (1) A region of low-temperature brittleness. For most metals this is below ordinary atmospheric temperatures. (2) An intermediate region above the temperature at which the metal becomes brittle due to cold, but below the temperature of recrystallization. It is in this temperature region that most metals are used. Mechanical working in this zone is called "cold working" and causes an increase in hardness and decrease in plasticity. (3) A zone of hot working, lying above the temperature of recrystallization. Metals possess little elasticity at these temperatures, but flow slowly under small loads. In this

zone mechanical working can be carried on to a practically unlimited extent.

The strength and hardness of metals normally decrease on raising the temperature, while the plasticity increases. Figure 67 shows the effect of temperature on the tensile strength, elongation, and reduction of area of copper. The elongation was measured on a gage length equal to 80 times the diameter of the specimen, so the values represent general elongation practically unaffected by the local stretch at the fracture. The results obtained at the higher temperatures depend largely on the rate of loading. The tests from which these curves are plotted were made in from 2 to 10 min.

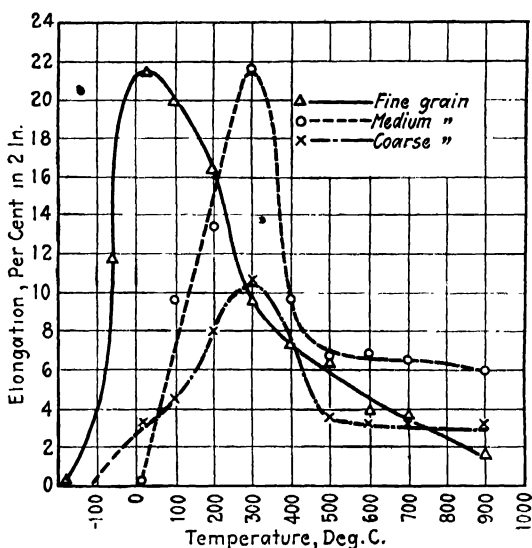


FIG. 68.—Effect of temperature on elongation of annealed molybdenum wire. (Sykes.)

Tensile strength decreases continuously from -185 to 950°C. , and is known to continue decreasing to the melting point ($1,083^{\circ}\text{C.}$).

Elongation also decreases continuously from -185°C. to the melting point. Throughout the same temperature range the plasticity *increases*, but elongation depends on both plasticity and strength; the decrease in elongation with rising temperature is due to the large decrease in tensile strength. Since the elonga-

tion has its highest value at the lowest temperature shown, it is obvious that the entire curve lies within the last two of the temperature regions mentioned above—i.e., the intermediate and the high. Copper probably enters the low-temperature zone of brittleness somewhere between -185° C. and absolute zero, but no actual tests are known to the authors.

Reduction of area increases slightly with rising temperature up to the temperature of recrystallization, above which it falls off sharply.

Tensile strength, elongation, and reduction of area are all increased to a marked extent by increasing the rate of loading when testing above the recrystallization temperature.

Figure 68 shows the effect of temperature on the elongation of annealed molybdenum. In these curves the low and intermediate temperature zones are represented. Recrystallization occurs at about 900° C., the highest temperature at which these tests were carried out. It is to be noted that the fine-grained wire retained its ductility at lower temperatures than the others.

Pressure.—Metals are perfectly elastic under pressure applied uniformly on all sides (under hydrostatic pressure). They are compressed as the pressure is applied but, on removal of the pressure, regain their original volume, except for the closing up of cavities. There is no permanent change in structure or properties. Hydrostatic pressure does not cause plastic deformation or cold-working effects.

Hardness increases with pressure, especially for soft materials. When a metal is under great hydrostatic pressure, its resistance to deformation is greater than at low pressures.

Metals are seldom used under hydrostatic pressures of any important magnitude, but such pressures are encountered in some fabricating processes. Extrusion is probably the best example. The metal is confined in a receiver, usually of cylindrical form, and pressed out through a die by a ram. Pressure is exerted on the metal on all sides except at the opening through which it is extruded. When a metal is worked in confined dies, as in swaging, and to a less extent in pressing and forging, it is under hydrostatic pressure, although there are of course, other forces which cause the desired deformations. Hydrostatic pressure acting on the metal in these fabricating processes contributes to its plasticity by holding the crystalline fragments in more intimate contact during deformation.

Elements of Structure.—The crystalline grains of a metal may vary as to size, shape, and orientation. Of these qualities, size¹ is by far the most definite. Shapes are so irregular that they are not subject to more than qualitative description. The most apparent distinction is perhaps that between equiaxed grains and elongated grains. In this connection it must be remembered that the elongated “grains” of a cold-worked metal are, in reality, aggregates of very small grain fragments. In a strictly pure metal, recrystallization ordinarily results in the formation of equiaxed grains. When sufficient insoluble (or soluble but segregated) impurities are present, there is a tendency for the grains to become longer in the direction of working. Elongated grains are also found in cast metal, especially after rapid solidification.

Grains also differ in shape with respect to their boundaries—whether made up of straight or of curved lines. Grain boundaries in ferrite (Alpha iron), for example, are normally quite curved and irregular, although they tend to become more rectilinear after certain annealing treatments. In Gamma iron and the austenitic solid solutions formed from it, the grain boundaries are, as a rule, straight and regular.

To describe the structure of a metal with reference to the orientation of its grains is still more indefinite. To begin with, it is quite difficult, or at least tedious, to determine the orientation of any particular grain. It seems that, ordinarily, the grains possess fairly well-mixed orientations. X-ray diffraction patterns show, however, that in severely cold-worked metals there is a tendency for the crystal fragments to assume a certain uniformity of orientation, which is found to persist after annealing. There is a peculiar type of “rectangular” brittleness sometimes encountered in annealed mild steel sheet which is attributed by Stead² to a more or less uniform orientation of the grains.

Fine grain is generally held to be a desirable structure, promoting toughness, strength, and ductility. Strength and hardness increase as grain size decreases, at least in the intermediate temperature zone. At high temperatures, fine grain is a source of softness, especially under prolonged application of load, which leads to flow at the grain boundaries. In general, small grain

¹ Methods of measuring and expressing grain size are described on page 89.

² STEAD, J. E., “Brittleness Produced in Soft Steel by Annealing,” *J. Iron Steel Inst.*, No. 11, pp. 137–184, 1898.

size contributes to hardness under conditions of temperature and rate of loading which lead to deformation by slip.

Plasticity decreases with decrease in grain size, in the sense that more effort is required to bring about a given deformation and that the strain-hardening effect of a given deformation increases. Malleability often increases as the grain size becomes smaller, however, because of the increased strength. Fine-grained zinc, for example, is malleable at ordinary temperatures, whereas coarse-grained zinc is brittle. Maximum ductility usually occurs at an intermediate grain size. Alpha brass, nickel-silver, and copper show maximum elongation at room temperature after an anneal well above the lowest recrystallization temperature, but well below the melting point, and hence with medium grain size. The reduction of area seems to be greater the finer the grain, within the limits of our ability to produce fine-grained recrystallized structures. There must be a limit to the reduction in grain size beyond which further refinement of grain will produce less reduction of area.

Deformation.—It is now known that cold deformation produces refinement of grain in the sense that one original grain, after cold work, exhibits a mixture of orientations.¹ This type of grain refinement is not the same as the refinement of grain produced by annealing at low temperatures. For example, a metal may be obtained with the same hardness by moderately cold working a coarse-grained piece or by annealing a severely worked piece at a temperature which will produce small unstrained grains. Although the hardnesses are the same, the other properties may not be and usually are not the same. These and other considerations make it necessary to consider that cold working produces a structure unlike that obtained in any other manner. Even though there is refinement of grain by cold working, the directional properties of the crystals are never obliterated, and, in fact, extreme conditions of cold work actually produce directional characteristics, namely, a tendency for the crystal units to be oriented in a certain manner with reference to the direction of deformation. This condition has been described by Berger² in very fine tungsten wire.

¹ BAIN, E. C. and JEFFRIES, ZAY, "Mixed Orientation Developed in Crystals of Ductile Metals by Plastic Deformations," *Chem. Met. Eng.*, vol. 25, p. 775, Oct. 26, 1921.

² Communication from laboratories of N. V. Phillips Lamp Factory, Eindhoven, Holland, *Physica*, vol. 1, p. 214, 1921.

Inasmuch as the structures produced by cold deformation are unique and are too minute for direct observation, the structural condition of cold-worked metals must be described in terms of the deformations to which they have been subjected.

The general effect of cold deformation is to increase hardness and decrease plasticity. The yield point and tensile strength are increased, and the elongation and reduction of area are

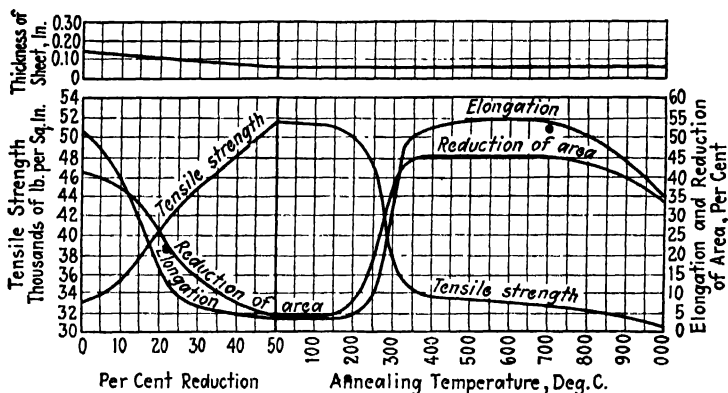


FIG. 69.—Effect of cold rolling and annealing on properties of copper. (Mathewson and Thalheimer.)

decreased. The capacity for further cold work is, of course, decreased. Annealing above the recrystallization temperature removes the hardening effects. Figure 69 shows the effect of progressive cold rolling on the properties of a very pure grade of copper. After being reduced cold 50 per cent in section, the metal was annealed at various temperatures, with the results shown on the right-hand side of the diagram.

In general, the effects of hot working are very much the same as those of cold working followed by annealing above the recrystallization temperature. Although at high temperatures metals are capable of some permanent deformation by the process of viscous flow at the grain boundaries, and perhaps migration of the boundaries themselves, most of the deformation incident to hot working takes place by the breaking up of the crystals and the movement of the fragments along the slip planes. This type of deformation produces conditions favorable to grain growth. Immediately after a deforming operation, such as a hammer blow or a pass through rolls, grain growth takes place in accordance with the temperature until interrupted by the next

deformation, which again breaks up the grains. The final grain size of hot-worked metal therefore depends largely upon the finishing temperature. A very high finishing temperature is apt to result in excessively coarse-grained metal. If, on the other hand, working is continued until the metal has cooled down around the recrystallization temperature, a somewhat strain-hardened condition may obtain.

Fiber.—Hot working creates “fiber.” Physical defects in a cast metal, such as blowholes, pipes, slag, or oxide films, are drawn out in the direction of working. The non-metallic impurities, being often brittle at the working temperature, are also to a large extent broken up and scattered. The result is a general improvement because of the greater continuity of the metal, and a special improvement in the direction of the working. The distribution of the impurities is such that their total cross-section on planes perpendicular to the direction of working is much less than on planes parallel to the direction of working. This may lead to quite appreciably lower physical properties—particularly elongation and reduction of area—in test bars taken at right angles to the direction of working, or “across the grain” of the metal. This effect is, of course, more marked the greater the amount of impurities present.

Impurities also affect the shapes of the grains. A perfectly pure and physically sound metal would, after hot working, have substantially equiaxed grains. Non-metallic impurities generally obstruct grain growth and, because of their distribution in worked metals, the obstruction to growth at right angles to the direction of working is greater than the obstruction to growth in the direction of working. The grains of hot-worked metals, or of metals that have been cold worked and annealed, therefore tend to be elongated in the direction of working.

Properties of Metal Crystals.—A single crystal is an aggregation of atoms occupying (or vibrating about) definite equilibrium positions, to which they tend to return if displaced by the application of an external force. This gives rise to the property of elasticity. The mathematical exactness of the space lattice results in a perfection of elasticity not attained in non-crystalline bodies. It may follow that single crystals are perfectly elastic. Any deformation short of rupture produced by an external force disappears on removal of the force. Furthermore, the extent of the deformation remains constant under a constant force—

that is, there is no flow in a single crystal. The rate of application and the duration of load, therefore, are of little significance, and return to the initial form on removal of load takes place very quickly with none of that "creep" shown by amorphous solids.

Failure of crystals under load seems always to take place on crystallographic planes, which are to be recognized as planes of weakness. If the fragments adhere to each other, the crystal is said to be plastic, and the planes of failure are slip planes or gliding planes. If the fragments do not adhere, the crystal is brittle and the planes are called "cleavage planes." In either case failure takes place by a shearing action, and the first failure marks the end of the single crystal. Up to this point the crystal is elastic. Therefore, the only "strength property" of a single crystal is its elastic limit in shear, which is, of course, different in different crystallographic directions. Hardness depends on the same property, since any method of hardness testing involves failure by shear. Conversely, the "strength" of single crystals, whether of pure metals or of metallic compounds, may be regarded as approximately proportional to their hardness.

Crystallization of a metal from the molten state is accompanied by the sudden development of a definite shearing strength. This strength increases as the temperature falls in a manner which, so far as is known, is continuous, unless there is an allotropic change. The strength of a crystal is evidently due to the attractive forces between its atoms. Thermal vibrations of the atoms oppose these attractive forces, so that at high temperatures the crystals are relatively soft and weak. As the temperature falls, the amplitude of atomic vibration decreases and the interatomic forces become more and more assertive, increasing the hardness and strength. Since the damping of atomic vibration is a continuous function of the temperature, the increase in strength of a single crystal on cooling must also be continuous, as long as there is no change in the arrangement of the atoms—that is, no allotropic change. The modulus of elasticity also increases continuously on cooling.

The properties of crystals of the various metals depend on the characteristics of the atoms of which they are built and on the type of space lattice in which the atoms are arranged. Only three types of lattice, all simple, have been found in most metals. These are the face-centered cubic, body-centered cubic (or centered cubic), and hexagonal close-packed. All metals known

to crystallize with the face-centered cubic arrangement are ductile throughout a wide range of temperature. Examples of this class are gold, silver, copper, and aluminum. The hexagonal arrangement appears less conducive to ductility, as illustrated by the metals, zinc, cadmium, and magnesium. Hull has pointed out that in the hexagonal arrangement there is only one set of planes parallel to which easy gliding or slip can take place, whereas in the face-centered cubic there are four. Both ductile and brittle metals are found with the body-centered cubic arrangement which seems somewhat less favorable to ductility than the face-centered.

Amorphous Metal.—There must, of necessity, be some disorganization of the crystalline structure at the grain boundaries of metals and on most of the surfaces of slip. The degree of disorganization probably varies all the way from perfect crystallinity to the completely disorganized structure denoted by the term "vitreous amorphous." All such metal of disorganized structure simulates the vitreous amorphous materials in its mechanical properties.

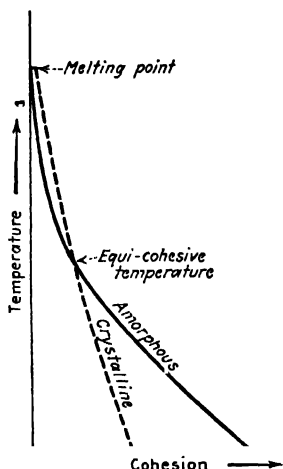


FIG. 70.—Cohesion-temperature relations of amorphous and crystalline metal.

Fluidity is the important characteristic of amorphous materials. Plastic deformation takes place by the same kind of flow as in ordinary liquids, except that at low temperatures the viscosity is very great. Whereas the strength of a crystal depends on temperature and is practically unaffected by the duration of loading, the resistance to deformation of an amorphous material not only varies rapidly with the temperature for a given rate or duration of loading, but if the temperature is constant depends entirely on the rate and duration of loading.

In Fig. 70 the two curves represent qualitatively the effect of temperature on the "cohesion" of crystalline and amorphous metal. For this purpose, cohesion of crystalline metal denotes the stress required to cause failure by slip. That is, cohesion is measured by the elastic limit of the crystal. Cohesion of amor-

phous metal is also measured by the elastic limit—*i.e.*, the maximum stress that can be sustained without permanent deformation. This quantity obviously depends on the time during which the stress acts. The curve, therefore, represents only one rate and duration of loading.

It will be noted that the crystalline metal is represented as acquiring a definite cohesion at the time of its formation—that is, at the freezing point of the metal—but there is no discontinuity in the cohesion of the amorphous metal at this point. Below the freezing point the cohesion of each modification increases continuously as the temperature falls, the rate of change being most rapid in the case of the amorphous metal. At some temperature the curves intersect, indicating that the cohesion of the amorphous modification has become equal to that of the crystalline. This temperature has been called the “equi-cohesive temperature.” As indicated above, the actual temperature depends on the rate and duration of loading. In general, it corresponds closely with the temperature of recrystallization. Above the equi-cohesive temperature the crystalline metal has the greater cohesion; below the equi-cohesive temperature the cohesion of the amorphous modification is the greater.

This conception is believed to be useful and suggestive in interpreting the properties of metals, but it must be remembered that it is qualitative rather than exact. It may be considered that, in general, the relative amount of amorphous metal increases with grain refinement and with cold working. It may also be considered that, in a qualitative way, the greater the amount of the amorphous modification present the more do the properties of a metal tend toward those of a vitreous amorphous material. For example, the property which metals have at high temperatures of yielding slowly under constant load is presumably due (at least in part) to the viscous flow of the disorganized metal at the grain boundaries. Since the amount of this disorganized or amorphous metal is greater in a fine-grained metal than in a coarse-grained metal, it would be expected that the fine-grained metal would be softer at high temperatures and harder at low.

Tensile Tests of Single Crystals.—Sykes¹ has described some very interesting tests of molybdenum wire in which many of the

¹ SYKES, W. P., “Effect of Temperature, Deformation, Grain Size and Rate of Loading on the Mechanical Properties of Metals,” *Trans. Am. Inst. Mining Eng.*, vol. 60, p. 780.

grains extended completely across the diameter of the wire (0.025 in.). At 200° C. and lower temperatures the path of rupture followed the grain boundaries. At 300 and up to 900° C., which is approximately the recrystallization temperature of molybdenum, the fracture was decidedly transcrystalline. In this temperature range, the wire drew down to a wedge at the fracture. The reduction of area was practically 100 per cent, but in one direction the diameter of the wire was scarcely reduced at all. This means that the deformation has been confined chiefly to two sets of slip planes.

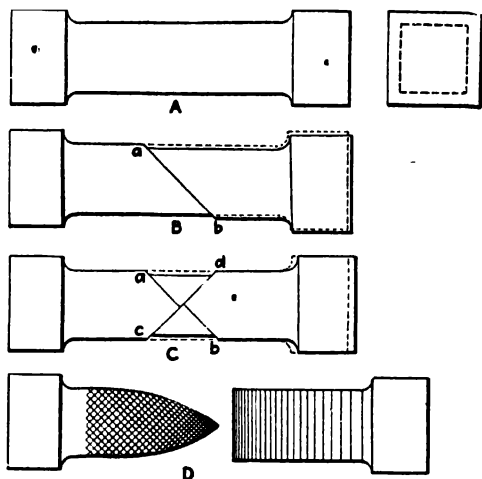


Fig. 71.—Plastic deformation of test bar composed of single ductile crystal.

The mechanism of deformation of a single crystal is illustrated schematically in Fig. 71, wherein A represents a test bar of square cross-section, consisting entirely of a single grain of a ductile metal. It is further supposed that this grain has such an orientation that planes of easy slip are perpendicular to the plane of the paper and make angles of about 45 deg. with the axis of the test piece. Now if the piece is subjected to tension, shearing stresses are developed which reach a maximum value at 45 deg. to the tensile load, and hence parallel to the planes of easy slip. As these stresses increase, failure of the crystal will take place in the form of slip, or block movement, along one of these planes, *ab*, the location of which will generally be determined by some local weakness (Fig. 71 B).

Ductile metals possess the property of automatically limiting the extent of the movement on any particular slip plane. Instead of slip continuing on the first plane until complete rupture of the piece occurs, the movement comes to a stop after a displacement which is very small as compared with the dimensions of the test piece. Resistance to movement along the first slip plane increases; further slip is forced to take place on new planes.

Let us suppose that the second slip is on a conjugate plane, cd , making an angle of about 90 deg. with the planes of the first set (Fig. 71 C). It is readily seen how repeated slips of this character result in a general increase in the length of the test bar and a decrease in its diameter.

Figure 71 D represents the test bar after rupture. The view on the left shows the same surface of the bar as in the three views above, and illustrates the multiplication of intersecting slip planes, especially near the fracture. The view on the right shows a face of the test bar at 90 deg. to that on the left. It will be noted that there has been no reduction in diameter on this face at the fracture. The test piece has drawn out into the shape of a wedge.

A remarkable study of single crystals of aluminum has been reported by Carpenter and Elam.¹ These investigators worked with flat test specimens 1 by 0.125 in. and with round specimens having diameters of 0.564 and 0.798 in. With each type of specimen they succeeded in converting the entire parallel portion into a single crystal.

The bars of circular cross-section, in which a single crystal occupied the entire cross-section, drew out into the form of wedges, as did Sykes' wires. Because of the much larger size of the aluminum bars, the edge of the wedge was not actually sharp, but retained a well-defined lens shape at the fracture. Reduction in diameter in the other direction was very slight.

Flat single-grain test specimens of aluminum assumed forms during deformation and fracture which varied widely with the orientations of the grains, as would be expected. In one type, the specimen became narrower, but retained practically its full thickness, while in a second type the specimen became thin, but retained substantially its original width. All bars were charac-

¹ CARPENTER, H. C. H. and ELAM, C. F., "The Production of Single Crystals of Aluminum and Their Tensile Properties," *Proc. Roy. Soc., A*, vol. 100, 1921; abstracted in *Chem. Met. Eng.*, vol. 26, p. 514, Mar. 15, 1922.

characterized by the small number of the systems of slip planes on which movement took place, and by a uniformity of direction of slip in any one grain.

Mark, Polanyi, and Schmid,¹ in Germany, studied the deformation of single crystals by means of x-ray crystal analysis. They found change of orientation at slip planes produced during the ordinary tensile test in single crystals of zinc. Conditions for maximum elongation of single crystals of zinc were determined. Zinc crystallizes with a hexagonal space lattice. The plane of easiest slip is the base of the unit hexagonal prism. When this plane makes an angle of approximately 45 deg. with the wire axis, the crystals are very ductile. Single crystal wires broken in tension at room temperature have shown as much as 600 per cent elongation; broken at 205° C., elongations up to 1,700 per cent have been obtained. Although zinc is not regarded as very ductile, these values for elongation are the highest of any known metal. Unless the plane of easiest slip is at an opportune angle with respect to the wire axis, the crystal is relatively brittle. Single crystal wires of bismuth were tested at 200° C. and showed up to 300 per cent elongation. In this case also the plane of easiest slip must make an angle with the wire axis of about 45 deg. or the crystal will be brittle when broken in tension. During the process of elongation of the zinc single crystals, the round wire changed into a flat ribbon. The width of the ribbon was at first slightly wider than the original diameter of the wire. Slip occurred in a plane about 45 deg. from the wire axis and extended across the whole cross-section of the wire in such a manner that the intersection of each slip plane with the wire surface formed an ellipse. The slight widening of the ribbon was due to the rotation of the elliptical sections. As the elongation increased, the general orientation of the crystal changed, so that the angles of the easiest planes of slip became more nearly parallel with the direction of extension.

In order that conclusions too sweeping may not be drawn from these phenomenal results on single crystals, it should be mentioned that the wires of zinc and bismuth were less than about 2 mm. in diameter and comparable results might not be expected in large single crystals. Fine tungsten wires composed of single crystals are sometimes ductile at ordinary temperatures,

¹ *Z. Physik.*, vol. 12, p. 58, 1922.

but larger single crystals have so far proved invariably brittle cold.

Support at Grain Boundaries.—The continuity of the planes of easy slip is broken at grain boundaries. Any movement of blocks or fragments of one grain is opposed by adjacent grains which, because of their different orientations, cannot yield easily in the same direction. Disorganized or amorphous metal which is probably present at the grain boundaries acts as an additional source of rigidity (at low temperatures). Above the recrystallization temperature flow takes place at the grain boundaries, so that they are sources of weakness rather than of strength.

The mutual supporting action of adjacent grains is shown clearly in Sykes' molybdenum wires (Fig. 72), where the grain boundaries stand out like joints in a piece of bamboo. It is evident that the supporting action is effective to a considerable distance within the grains. A shortening of such grains would therefore be expected to result in an increase in strength, even though they still extended across the entire section of the wire. When the number of grains on the cross-section is also increased, the supporting action becomes still greater. Thus at 300° C., Sykes obtained the following values for tensile strength vs. grain size:



FIG. 72. — Fracture of coarse-grained molybdenum wire broken in tension. (Sykes.)

AVERAGE GRAIN DIAMETER	TENSILE STRENGTH, POUNDS PER SQUARE INCH
Single grain.....	32,000
0.0011 in.....	51,000
0.0002 in.....	96,000

This increase in strength (and hardness) with decrease in grain size is characteristic of metals below their recrystallization

temperatures. The quantitative relation of strength to grain size varies with the metal involved, the temperature of test, the rate of loading, and the size of the piece, since it is not only a question of absolute grain size but also of the number of grains on the cross section. When the number of grains on the cross-section is fairly large, however (say 1,000 or more), the absolute grain size is the important thing.

In the tests reported by Carpenter and Elam, which were carried out at room temperature, the tensile strength of single crystals of aluminum of 99.6 per cent purity was found to vary from 6,270 to 9,180 lb. per square inch. The same material treated to produce an average grain diameter of 0.0667 in. had a tensile strength of 10,440 lb. per square inch, an increase of 66.5 per cent over the lowest and 13.7 per cent over the highest value for the single grains.

A most thorough correlation of grain size and Brinell hardness, measured at room temperature, has been worked out for Alpha brass (68:32) by Bassett and Davis.¹ This alloy consists structurally of a single homogeneous solid solution, and is quite comparable to a pure metal. Some typical values obtained in one series were:

AVERAGE GRAIN DIAMETER, INCH	BRINELL HARDNESS
0.01400	41.7
0.00460	49.2
0.00300	52.4
0.00140	62.4
0.00093	77.4

Observers are sometimes surprised to find that a very apparent difference in the grain size of two specimens is not accompanied by any marked difference in hardness. Referring to the second and third specimens in the table above, it will be seen that an increase in grain diameter of over 50 per cent has decreased the hardness only about 6 per cent. The difference in grain size would be quite apparent under the microscope, while the difference in hardness would be noticed only by measurements made with rather more than ordinary care. On the other hand, a similar increase in grain size between the last two specimens is

¹ BASSETT, W. H. and DAVIS, C. H., "A Comparison of Grain Size Measurements and Brinell Hardness of Cartridge Brass," *Trans. Am. Inst. Mining Eng.*, vol. 60, p. 428.

accompanied by a marked difference in hardness. The effect of a given percentage difference in grain size is greater the smaller the grains.

Grain Size vs. Hardness at Higher Temperatures.—When ductile metals are broken "cold"—that is, below their recrystallization temperatures—fracture normally takes place through the grains and avoids the grain boundaries. At temperatures just under the melting point, metals are quite weak and fracture is intergranular. There is a range of temperature above that of recrystallization in which either transcrystalline or intergranular fracture may be produced at will by varying the rate of loading and duration of load. Slow loading and prolonged application of load favor intergranular fracture at low unit stress. Under these conditions the grain boundaries are sources of weakness rather than of strength. Accordingly, at high temperatures the relation between strength and grain size is reversed, and the large-grained specimens are the harder. There must then be an intermediate temperature at which strength and hardness are little affected by grain size. This is the "equi-cohesive temperature." The following account of some experiments is taken from a paper by one of the authors:¹

Tests have been made on iron, tungsten, platinum, gold and silver. Small wires of these metals were drawn to a diameter of 7 to 8 mils in such a manner that the structures were fibrous—that is to say, a considerable amount of working on these metals was performed at temperatures below their annealing temperatures. Some pieces of each of the wires were heated by the passage of electric current, the temperature and time conditions being maintained in such a manner as to cause recrystallization and to produce one set of each of the metals composed of small equiaxed grains and another set composed of large equiaxed grains. The fine-grained and coarse-grained samples of the same material were compared with respect to the resistance to bending at various temperatures. Small hairpins were formed from each of the wires. Let us take the pair of silver wires as an example. The arms of each hairpin were 2 in. long and the distance between the two ends was $\frac{3}{4}$ in. A clamp consisting of two steel bars was used to hold the hairpins. Two hairpins, one of fine-grained and the other of coarse-grained silver wire, were put in the clamp a short distance apart. It was found that a rider weighing 0.2 gram suspended on the ends of the hairpins would not cause a permanent deformation in either the fine-grained or coarse-grained samples at room temperature, but would

¹ JEFFRIES, ZAY, "The Amorphous Metal Hypothesis and Equi-cohesive Temperatures," *J. Am. Inst. Metals*, vol. 11, p. 300.

cause permanent deformation of the wires at slightly higher temperatures. The steel clamp holding the two silver hairpins in a horizontal position was inserted in a muffle furnace and the temperature was gradually raised. At temperatures lower than 250 to 275° C. the fine-

TABLE VII

Kind of wire	Diameter, inch	Equicohesive temperature, degrees Centigrade
Iron.....	0.0070	550 to 600
Tungsten.....	0.0070	1,350
Silver.....	0.0075	250 to 275
Gold.....	0.0085	275 to 300
Platinum.....	0.0075	525 to 550

grained silver wire was the stronger—that is, it would hold the given weight with less deformation or bending than would the coarse-grained silver wire. Above 275°, however, the fine-grained silver wire had been deformed or bent to a greater extent than the coarse-grained one. The conclusion is that the fine-grained and coarse-grained silver had the same resistance to deformation at 250 to 275° C., that at temperatures less than this the fine-grained silver has the greater resistance to deformation, while at higher temperatures the coarse-grained silver has the greater resistance to deformation. These tests were performed with the other metals named and the results are given in Table VII. The iron and tungsten wires were heated with electric current in an atmosphere of hydrogen in order to prevent oxidation. The temperatures were measured with an optical pyrometer. The gold and platinum wires were heated in a muffle, the same as the silver, and the temperatures were measured with a thermocouple.

The wires used for the hairpin tests were examined microscopically to make certain that the heat treatment had produced the desired grain size. The fine-grained wires were made by heating the cold-worked wires quickly to a temperature considerably above that of recrystallization and the coarse-grained samples were produced by heating slowly through the recrystallization range followed by heating to a temperature near the melting point. The heating was done by passing electric current through the wires.

It will be noted that the equi-cohesive temperatures found for these metals correspond closely with their respective temperatures of recrystallization. This relation is a general one, having been found to hold for all metals investigated. Some experi-

ments on zinc, lead and tin, which recrystallize at or below room temperature, are interesting. Quoting again from the paper mentioned above:

Some pure zinc, lead, tin and aluminum were cast in such a manner as to produce coarse-grained structures. One piece of each of the castings was tested for Brinell hardness as cast and one piece of each was cold-hammered, after which the Brinell hardness was determined. The cold-hammering of the zinc was continued until cracks began to form at the edges of the piece. In testing for hardness, 500 kg. pressure was used with the zinc and aluminum, 200 kg. with the tin, and 100 kg. with the lead.

It was noticed with all of the samples with the exception of the aluminum, that when the load was brought up to the required amount the beam of the balancing mechanism of the Brinell machine would very quickly fall. When the pressure was again brought up to that required, say for the zinc 500 kg., the beam would again drop. This means that the pieces of lead, zinc and tin were gradually deforming under constant load. The pressure was maintained at the required amount until the beam at a constant position of the specimen table would remain in a substantially constant position.

With both cast and cold-hammered aluminum, the beam remained in a substantially constant position after the load was first brought to the required amount. A very slight lowering was noticed, but the effect of increasing the time of exposure of a given load was practically nil on the resulting hardness.

This slow deformation was the most marked in the tin. It was more pronounced in the cold-hammered samples than in the cast samples and the maximum effect was found in the cold-hammered tin. When the hardness tests were carried on in such a manner that there was substantially no further deformation in the pieces of metal with constant load, it was found that the cold-hammered aluminum was harder than the cast aluminum, whereas the cold-hammered lead, tin and zinc were all softer than the same metals in the cast state.

To obtain an idea of the rate of deformation of the pieces of lead, tin and zinc, the diameter of the impression of the ball of the Brinell hardness machine was measured on each of the samples after the load had first registered the required amount. For example, the tests on zinc were made as follows:

The piece of cast zinc was put in the Brinell machine and the pressure raised quickly to 500 kg. Then the piece of cold-hammered zinc was inserted in the machine and the pressure raised to 500 kg., the rate of application of the load being the same in both cases. The hardness numbers were then calculated. It was found that the hardness of the cold-hammered pieces of aluminum, zinc, lead and tin was greater

when determined in the above manner than that of the same metals in the cast state. The results of the hardness tests are given in Table VIII.

TABLE VIII.—HARDNESS OF WHITE METALS, CAST AND HAMMERED

Material	Pressure in kilo- grams	Load sustained		Quick release of load	
		Diameter of im- pression in milli- meters	Hard- ness	Diameter of im- pression in milli- meters	Hard- ness
Cast aluminum.....	500	4.75	26.50	4.75	26.50
Cold-hammered aluminum..	500	3.70	44.80	3.70	44.80
Cast zinc.....	500	4.15	35.30	3.65	46.20
Cold-hammered zinc....	500	4.20	34.50	2.90	74.00
Cast lead.....	100	4.85	5 10	4.70	5.44
Cold-hammered lead.	100	5.05	4.66	4.30	6.54
Cast tin.....	200	5.65	7.30	5 10	9.12
Cold-hammered tin	200	6 80	4.72	4.60	11.32

It is known that the equiaxing temperature of zinc after severe cold-work is not far below room temperature, and the hardness results would indicate that the equi-cohesive temperature of zinc would be only slightly below room temperature. The equiaxing temperatures of severely cold-worked lead and tin are considerably below room temperature, and the hardness results given in Table VIII would indicate that their equi-cohesive temperatures would also be considerably below room temperature. The equiaxing temperature of severely cold-worked aluminum is about 200° C. with 1 hour's exposure at that temperature. The hardness results in Table VIII show that the equi-cohesive temperature of aluminum must be considerably above room temperature.

The lead and tin referred to as "cold-hammered" were found by microscopic examination to be fully recrystallized, and therefore representative of normal fine-grained metal as distinguished from the coarse-grained cast specimens. It may be added that the duration of "sustained" load in the tests reported in Table VIII was about 15 min. for the aluminum and about 1 hr. for each of the other metals, while "quick release" was in each case after approximately 10 sec.

These results bring out in a striking way the fact that the equi-cohesive temperature, as well as the recrystallization temperature, is dependent on the time factor. The temperatures

at which the Brinell hardness is independent of the grain size are; for lead and tin, above room temperature for rapid loading but below room temperature for slow or prolonged loading. The equi-cohesive temperature of copper has been found to lie above 950° C. for rates of loading producing rupture in about 3 sec., whereas for very slow loading it is in the neighborhood of 300° C. In general, the equi-cohesive temperature is higher the more rapid the application and the shorter the duration of load.

Grain Size vs. Elongation.—The elongation found on single-crystal test bars of aluminum by Carpenter and Elam ran up to 87 per cent, as compared with about 37 per cent on bars with an average grain diameter of 0.0067 in. When there were two or three crystals on the cross-section, the elongation was less than 87 per cent, but greater than the elongation on the fine-grained bars. In Sykes' tests on molybdenum wires, on the other hand, the elongation was less on the wires composed largely of single crystals than on other wires of smaller grain size. These results are not contradictory, as the conditions of test were different. The gage length of the molybdenum wires was 80 times the diameter, and the elongation measured was the general elongation. Furthermore, the gage length included several grain boundaries, at which, as was seen in Fig. 72, the deformation was relatively slight. Carpenter and Elam used test bars in which the ratio of gage length to cross-section was relatively small, so the measured elongation was greatly increased by the high reduction of area, and the gage length consisted entirely of a single crystal. If the elongation on the molybdenum wires had been measured over the single crystal in which the break occurred, the per cent elongation would have been much higher. Unfortunately, no tests have been made on single crystals having a sufficiently great ratio of gage length to diameter so that the general elongation could be measured, unaffected by the local stretch.

In general, the grain size conducive to maximum elongation is neither extremely fine nor extremely coarse. The actual grain size which will give the highest elongation for any particular metal depends on the size and shape of test piece, the temperature of test, and rate of loading. Curves given in Fig. 68 show how the relation between grain size and elongation in molybdenum depends on the temperature. The fine-grained wire, which had the greatest elongation at temperatures below 200° C., had the least elongation at 900° C.

3 The effect of grain size and diameter of test specimen on the elongation and reduction of area of Armco iron is shown in Table IX.

TABLE IX.—EFFECT OF DIAMETER AND GRAIN SIZE ON TENSILE PROPERTIES OF ANNEALED ARMCO IRON

Diameter, inch	Grains per square incl.	Tensile strength, pounds per square inch	Elongation, per cent in 2 in	Reduction of area, per cent	Number of grains across diameter of wire
0.204	400	41,000	30.0	76	100
0.025	810	48,550	12.5	76	18
0.023	2,680	48,200	23.7	78	30

Table X shows the required tensile strength and elongation of annealed copper wires of various diameters as specified by the American Society for Testing Materials.

TABLE X.—TENSILE STRENGTH AND ELONGATION REQUIRED IN SOFT ANNEALED COPPER WIRE

Diameter, inch	Tensile strength, pounds per square inch	Elongation, per cent in 10 in.
0.460 to 0.290	36,000	35
0.289 to 0.103	37,000	30
0.102 to 0.021	38,500	25
0.020 to 0.003	40,000	20

Lower elongation in small wire and thin sheet or strip is a general observation in metals. But, as shown in Table IX, a small grain size seems conducive to high elongation in small wire or thin strip.

Brittleness.—Brittleness in metals may be due either to brittleness of the grain boundaries or to lack of plasticity in the crystals themselves. Equiaxed tungsten breaks in a brittle manner at temperatures below 200° C., the fracture taking place almost entirely at the grain boundaries. Individual crystals of tungsten appear to be somewhat plastic. The low-temperature brittleness is therefore due to brittleness at the grain boundaries, a condition which is consistent with the view that the grain boundary metal is

amorphous and that the amorphous metal increases in hardness⁴ and brittleness, as the temperature is lowered, more rapidly than does the crystalline. Coarse-grained zinc is but slightly ductile at room temperature, whereas fine-grained zinc may have an elongation as high as 90 per cent. In the coarse-grained zinc, the fracture takes place largely through the grains. Both fine-grained and coarse-grained zinc are brittle in liquid air, the fracture again taking place chiefly through the grains. Brittleness in this case is therefore due to lack of plasticity in the crystalline grains themselves. In either case small grain size favors the retention of ductility at low temperatures.

Reduction of Area.—The first yielding of a tensile test bar of a ductile metal involves a local reduction in the cross-sectional area. The stress intensity at this point is then higher than in the rest of the bar, which has not yet yielded. If it were not for the work-hardening effect of this slight local deformation, the reduced section would not be able to sustain a load sufficient to deform the remainder of the bar, so the section would continue to reduce, and rupture would finally occur at this point, without any general extension of the bar as a whole.

A certain minimum rate of work hardening is necessary for general extension to take place. Suppose the first local yielding reduces the cross-section of the bar by 1 per cent. Then, unless the yield point of the metal is raised slightly more than 1 per cent by this deformation, the reduced section will not be able to sustain even the load which originally caused it to yield, and which was *insufficient* to cause yielding in the remainder of the bar. If the yield point is raised more than 1 per cent, then an increase in load will cause further deformation to occur at some other point in the bar. This process results in general extension, or general elongation.

Usually a stage is reached at which the rate of hardening is not sufficient to shift automatically the location of the yielding. The bar then necks down and breaks.

As long as general extension is taking place, the *load* on the bar must be increasing. When necking begins, the load can no longer increase. It may remain fairly constant for a while and must then decrease. The load per unit area of the reduced section, however, may continue to increase.

The total reduction of area at fracture is thus made up of two parts: (1) A reduction corresponding to the general extension

before necking begins—the volume of the metal remains practically constant; (2) a local contraction at the point of fracture.

It will thus be seen that a rapid rate of hardening by deformation favors general extension rather than local reduction of area. Manganese steel is a typical example of a material which shows a high general elongation with little local reduction. It is also characterized by rapid hardening under deformation. Bronze behaves in a similar manner. Brass shows a greater tendency to neck down, but much less so than pure copper, which hardens less rapidly by deformation.

An extreme case is represented by glass at such a temperature that it is fairly soft. Pulling a glass rod in this condition results in a break with practically 100 per cent reduction of area and little general elongation. The glass does not become harder as a result of the deformation. If a hot rod of glass is withdrawn from the source of heat and pulled apart, there is apt to be very high general extension, because the points which are reduced in cross-section strengthen themselves by becoming cooler. If they remained at the same temperature, rupture would occur at the first point to yield and general drawing out would not be possible.

At high temperatures, metals somewhat resemble soft glass, since the hardening effect of the deformation is removed by spontaneous annealing. Some annealed copper wires tested at room temperature showed a general elongation of 24.5 per cent with a reduction of area of 76 per cent. When broken at 950°C. at such a rate that rupture occurred in 5 sec., the elongation was 17 per cent and reduction of area 98 per cent, a considerable increase in reduction of area with a decrease in elongation.

Reduction of area of single crystals tested in the intermediate zone of temperature is very high, approaching in some cases 100 per cent. On the other hand, when there are a small number of grains to the cross-section of a test piece, conditions appear to be unfavorable for high reduction of area. If the grain size becomes still smaller, the reduction of area increases. Extremely small grain size, such as probably exists in hardened steel, is unfavorable to plasticity of any kind, so that, theoretically, a point must be reached where further reduction of grain size no longer results in increased reduction of area in the tensile test. This point is apparently not reached in recrystallized metals; ordinarily, the reduction of area is greater the smaller the grain size.

Overstrain in Iron and Steel.—When hot-rolled iron or mild steel is tested in tension, it is found that the first part of the stress-strain diagram is a straight line, representing elastic deformation up to roughly one-half the tensile strength. If a bar of such material is loaded to a stress well beyond its yield point, it will be found, on removal of the load, to have lost its elasticity. On a second application of the load, the stress-strain diagram curves away from the straight line representing proportional deformation; the proportional (or elastic) limit has been reduced

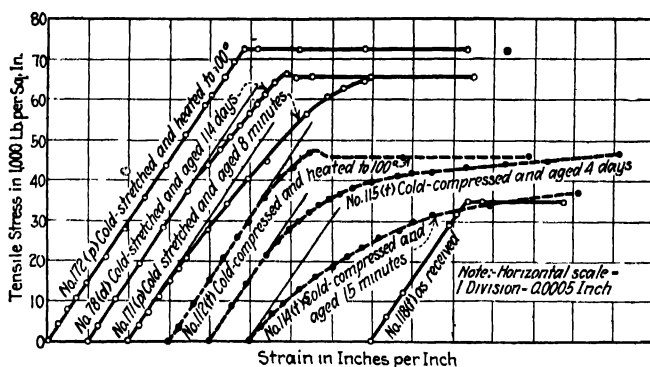


FIG. 73.—Effect of aging and tempering on the elastic properties of cold-worked mild steel. (*Van Den Broek.*)

practically to zero. If, after the first loading beyond the yield point (overstraining), the bar is permitted to rest for a few weeks before the second tensile test, it will then be found to have recovered its elasticity, and may have a new proportional limit higher than the original proportional limit of the hot-rolled material.

This recovery of elasticity takes place slowly at ordinary temperatures, but more rapidly as the temperature is raised. Muir found that the recovery of elasticity at 100° C. is as complete after a few minutes as in 2 weeks at room temperature. At 250° C. the time required is measured in seconds or fractions.

While the proportional limit in tension can be greatly increased (approximately doubled) by overstrain in tension, followed by aging or heating at low temperatures, the limit in compression is not similarly increased. In fact, it has been stated that the gain in tensile proportional limit is almost exactly compensated by loss in compressive proportional limit, so that the total elastic

range is not greatly changed. Van den Broek¹ has reported, however, that, by stretching and reheating, the proportional limit of mild steel in tension can be about doubled, while still retaining approximately the original proportional limit in compression. In Fig. 73 the effects of aging and tempering are shown. Curve No. 118 shows the elastic properties of a hot-rolled low-carbon steel. Curves 114 and 171 show how the elastic limit in tension is reduced practically to zero by cold deformation, either in tension or compression. The other curves illustrate the recovery of elasticity by aging and by heating to 100° C. The elastic limit in tension of the steel which was compressed and heated to 100° C. has not quite been restored to its original value, but it is possible it would upon further heating.

Recovery of elasticity on aging at ordinary temperatures or on heating at temperatures up to about 300° C. is accompanied by increase in hardness and tensile strength and by loss of plasticity. Elongation is usually reduced to a marked extent, although the reduction of area is less affected. The change that takes place, is, therefore, a general hardening and stiffening.

Blue Heat Phenomena in Iron:—It has long been known that iron is peculiarly brittle at temperatures from 200 to 400° C., and that deformation, such as bending, effected at these temperatures causes the metal to be much more brittle after cooling to room temperature than would a similar amount of deformation at room temperature. Because of the blue scale or temper color formed on iron and steel, this temperature range is commonly called a "blue heat," and the brittleness is called "blue brittleness."

Tensile tests at elevated temperatures show that iron actually has a higher tensile strength but lower elongation and reduction of area in the blue heat range than at room temperature. The curves in Fig. 74 show the results of tests at the U. S. Bureau of Standards² on a mild steel whose properties are essentially those of iron. Results of a similar nature have been reported by one of the authors,³ and are reproduced in Fig. 75. Robin has shown

¹ VAN DEN BROEK, J. A., "The Effects of Cold-working on the Elastic Properties of Steel," *Carnegie Scholarship Memoirs, Iron & Steel Inst.*, vol. 9; also *Engineering*, July, 1918.

² FRENCH, H. J., "Strength and Elasticity of Boiler Plate at Elevated Temperatures," *Chem. Met. Eng.*, vol. 26, p. 1207.

³ JEFFRIES, ZAY, "Effect of Temperature, Deformation and Grain Size on the Mechanical Properties of Metals," *Trans. Am. Inst. Mining Eng.*, vol. 60, p. 474.

that the Brinell hardness is also greater at a blue heat than at room temperature.

The fact that a given amount of deformation effected at a blue heat hardens iron to a greater extent than does the same amount

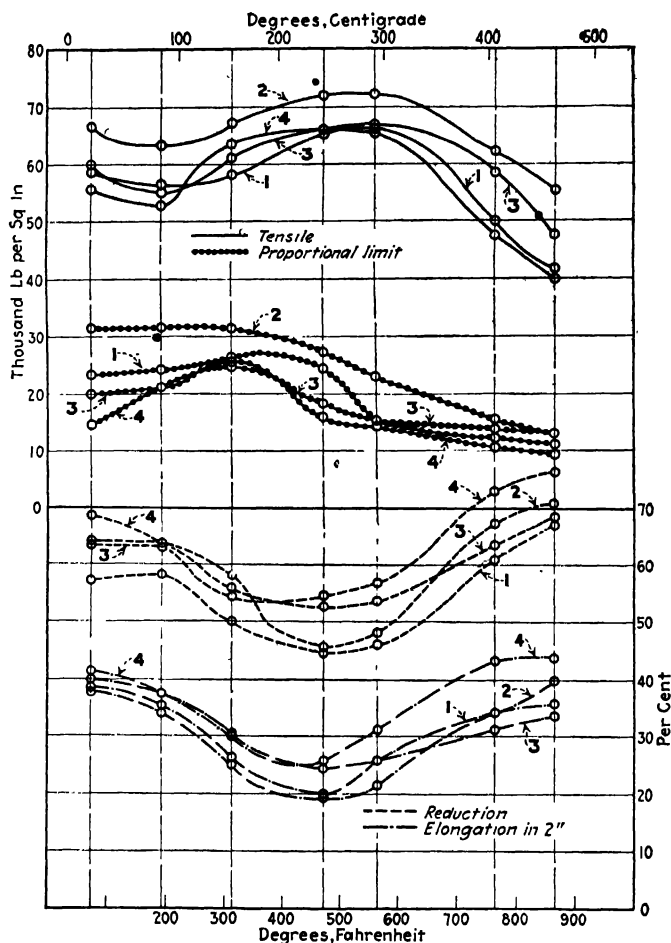


FIG. 74.—Effect of temperature on tensile properties of mild steel. (French.)

of deformation effected at room temperature is illustrated nicely by some experiments on the drawing of Armco iron wires. For example, wires reduced cold from 0.042 to 0.025 in. (64 per cent) at room temperature and at 275° C. had the following tensile properties (measured at room temperature):

TEMPERATURE OF DRAWING	TENSILE STRENGTH, POUNDS PER SQUARE INCH	ELONGATION, PER CENT	REDUCTION OF AREA PER CENT
Room temperature.....	85,720	2.60	70
275° C.....	111,000	1.58	67

The wire drawn at blue heat is stronger and less plastic than that drawn at room temperature.

Years ago Le Chatelier¹ observed that the tensile properties of iron in the blue heat range are greatly affected by the rate of

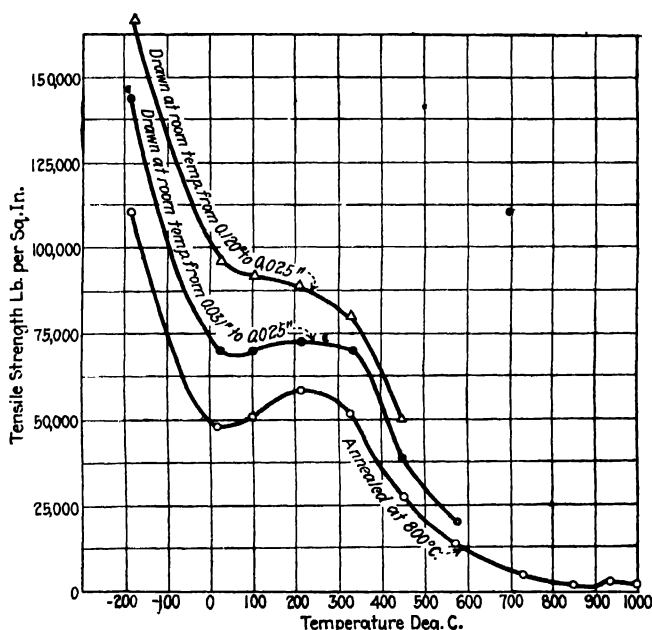


FIG. 75.—Effect of temperature on the tensile properties of annealed and cold-drawn Armeo iron wires.

application of load. One specimen, for example, had a tensile strength of 66,850 lb. per square inch and an elongation of 10 per cent when broken in 20 min. at a temperature of 170° C. On increasing the rate of loading until fracture occurred in 2 sec. the tensile strength fell to 38,400 lb. per square inch, while the elongation rose to 28 per cent. The general result of his researches follows:

¹ Abstracted in FETTWEIS, "The Blue Brittleness and Aging of Iron," *Stahl u. Eisen*, Jan. 2 and Jan. 9, 1919.

With various rates of applying load, the curves which give the tensile properties of iron as functions of temperature are approximately the same shape, but when testing at higher speeds, the curves are shifted toward higher temperatures. In other words, the maximum in strength and hardness does not occur at a fixed temperature, but at a temperature which depends on the rate of loading and is higher as that rate increases.

To explain these phenomena, Le Chatelier postulated that, at temperatures above about 80° C., any permanent deformation of iron gives rise to an irreversible transformation which tends to raise the tensile strength and decrease the ductility. This transformation requires a certain amount of time for its complete development, but takes place more quickly the higher the temperature. Above 300° C., however, the transformation is less effective in producing strength and hardness, because of incipient annealing.

In a paper published in January, 1919, by Fettweis,¹ this transformation of Le Chatelier is, apparently for the first time, identified with the transformation responsible for elastic recovery after overstrain. Fettweis did not propose any hypothesis as to the mechanism of this transformation.

In February, 1920, one of the present authors² independently stated the theory that the blue heat phenomena and elastic recovery are due to the same cause—a spontaneous increase in resistance to motion on the slip planes formed during deformation.

It is supposed that immediately after motion begins on a slip plane the resistance is less than the shearing strength of the unbroken crystals. Deformation tends to progress by continued motion on this plane, until brought to a halt by end resistance—that is, by the interference of adjacent grains. If the deforming load is removed immediately after slip has started and time is allowed for elastic recovery, then the resistance to motion on the plane of slip spontaneously increases to a value equal to or greater than the resistance to the formation of a new slip plane. Further deformation must then take place on new planes. The time required for this increase in resistance is less as the temperature rises, so that at about 250 to 300° C. the change is

¹ See note 1, page 184.

² Discussion by R. S. Archer, on paper "Physical Changes in Iron and Steel Below the Thermal Critical Range," Zay Jeffries, February, 1920, meeting A.I.M.E.

practically instantaneous and occurs during the progress of any ordinary deformation such as a tensile test. The result is that at a blue heat a given *external* deformation produces more internal deformation, or cold working, and hence more *hardening*, than the same amount of external deformation effected at room temperature.

This statement applies to deformations effected within a short period of time, such as during an ordinary tensile test. If the deformation which takes place during the tensile test at room temperature could be effected very slowly, so that there was time for elastic recovery during the test, it would be expected that the tensile strength would increase to an extent comparable with the increase obtained at a blue heat. The following experiments made by J. T. Bottomley¹ in Lord Kelvin's laboratory confirm this expectation:

Eight pieces of soft iron wire were tested in tension by gradually increasing stress applied in 10 min. of time in each case. They broke at loads of 43.5 to 46 lb. (average 45.2 lb.), with 17 to 22 per cent elongation. Another specimen left with 43 lb. hanging on it for 24 hr. and then broken by gradual increase of stress during 25 min., broke at a load of 49.25 lb. with 15 per cent elongation. Another left for 3 days with 43 lb. hanging on it, and then broken by increasing stress, bore 51.5 lb. and elongated 14.4 per cent. A wire loaded first with 40 lb. and broken with gradual addition of load in 2 months broke at 57.25 lb. The slower loading had, therefore, increased the strength by about 27 per cent, which is an increase of the same order of magnitude as that obtained by testing in the blue heat range with ordinary rates of applying load.

According to the theory here described, the blue heat properties of iron are due to certain peculiarities of the process of deformation, and are not specific properties of crystalline iron. The yield point, tensile strength, Brinell hardness, elongation, and reduction of area are all properties whose measurement necessarily involves plastic deformation. The true elastic limit, on the other hand, being the stress at which plastic deformation begins, cannot be affected by the mechanism described, nor can the modulus of elasticity. Unless there is an allotropic change (change in atomic arrangement), it is to be expected

¹ UNWIN, "The Testing of Materials of Construction," 3rd ed., p. 113.

that both elastic limit and elastic modulus will decrease continuously as the temperature rises.

There is a lack of sustaining evidence of any allotropic change in these temperature regions, and recently E. C. Bain has found by *x*-ray analysis that iron at 300° C. has the same body-centered cubic lattice as at room temperature.

Actual determinations of elastic limit by various investigators are not in good agreement. Howard¹ in 1890 reported that the elastic limit decreases with rise in temperature. Huntington² also gave a curve which does not pass through any maximum in the blue heat range. Martens,³ however, reported that the elastic limit passes through a maximum at about 200° C., and recently H. J. French⁴ found a maximum value at 200° C. about 14 per cent greater than at room temperature. Accurate determination of proportional or elastic limit at the higher temperatures is a matter of some experimental difficulty, and, in fact, the values found in any determination depend on the sensitivity of the instruments. From the sufficiency of the deformation theory in explaining the other blue heat properties and the evidence against an allotropic change, it is very probable that the "elastic limit" which increases in the blue heat range involves some plastic deformation and that more sensitive measurements would show a continuous decrease in elastic limit and elastic modulus. The rise in tensile strength at a blue heat is most pronounced for iron in the annealed condition. Such strengthening becomes less in cold-worked iron tested at a blue heat, and, finally, in iron severely cold-worked and aged for some time, the tensile strength at room temperature is greater than at any higher temperature. This simply means that, because of the great hardening already obtained by cold working and aging, the hardening effect of the relatively small deformation occurring during the tensile test is not sufficient to compensate for the natural loss of cohesion due to the rise in temperature. Furthermore, heating to temperatures as low as 100° C. produces a slight softening in iron which has been severely cold worked and aged.

¹ HOWARD, J. E., "Physical Properties of Iron and Steel at Higher Temperatures," *Iron Age*, vol. 45, p. 585, 1890.

² HUNTINGTON, A. K., "Effect of Temperature on Tensile Tests of Copper and Its Alloys," *J. Inst. Metals*, vol. 8, p. 126, 1912.

³ MARTENS, "Influence of Heat on the Strength of Iron," *Proc. Inst. Civil Eng.*, vol. 104, p. 209, 1890-1891.

⁴ See note 2, page 182.

Overstrain in Non-ferrous Metals.—Iron appears to be unique in the magnitude of the overstrain and blue heat phenomena, but similar properties have been observed in some other metals.

It has been found that the tensile strength vs. temperature curve for nickel exhibits a horizontal portion between 200 and 300° C., although the tensile strength does not actually rise in this region. There is a corresponding drop in elongation and reduction of area. This has been attributed to the allotropic change in nickel supposed to correspond to the magnetic change at 320°, but recently the space lattice of nickel at 500° has been determined by E. C. Bain and found to be the same as at room temperature. The magnetic change is, therefore, not due to allotropy (in the sense of atomic rearrangement). In view of the properties of

TABLE XI.—STRENGTHENING OF NICKEL WIRE AT 250 TO 275° C.

Treatment of specimens	Tensile strength, pounds per square inch	Per cent increase
Kept in liquid air until tested, 15 min. after drawing	125,000	
Kept in liquid air until tested, 15 min. after drawing	126,000	
Kept in liquid air until tested, 15 min. after drawing	126,000	
Kept in liquid air until tested, 15 min. after drawing	126,000	
Average.....	125,750	
Heated at 275° C. 2 min.	130,500	3.10
Heated at 275° C. 5 min.	132,000	4.60
Heated at 275° C. 10 min	130,000	
Heated at 275° C. 30 min.	131,000	
Kept in liquid air until tested, 45 min. after drawing	126,000	
Heated at 250° C. 1 min.	128,000	1.60
Heated at 250° C. 2 min.	128,000	1.60
Heated at 250° C. 5 min.	128,000	1.60
Heated at 250° C. 20 min	130,000	3.20
Kept in liquid air until tested, 2 hr. after drawing. .	125,000	
Heated at 250° C. 5 min.	128,000	2.45
Heated at 250° C. 15 min.	130,500	4.00
Heated at 250° C. 3 hr. :	127,000	

iron, it seemed probable that the break in the tensile strength-temperature curve of nickel was due to the same sort of spontaneous hardening.

W. P. Sykes has recently made some tests which show that freshly cold-drawn nickel wires are hardened by heating at 250 and 275° C. His results are given in Table XI. The nickel wire was drawn cold from 0.090 to 0.025 in. diameter. This wire was immersed in liquid air immediately after coming through the finishing die and kept in liquid air until tested or put in an electric muffle furnace for heat treatment as designated in the table. Immersion in liquid air was for the purpose of preventing the hardening process from taking place, as it is known that in iron the change is extremely slow at low temperatures.

Price and Davidson¹ have also reported a hardening effect on heating cold-rolled nickel at temperatures up to 450° C. Brinell hardness of bars cold rolled from 0.5 to 0.134 in. was as follows:

As rolled.....	235
Heated to 250° C	262
Heated to 350° C.....	255
Heated to 450° C	248
Heated to 550° C.....	228

The heating time was ½ hr. to reach temperature plus 25 min. at heat in all cases. A maximum strengthening effect was found in longitudinal specimens after heating at 250° C., the strength increasing from about 123,000 to 134,000 lb. per square inch.

It has been reported that the first effect of annealing cold-worked copper and aluminum at low temperatures is to increase the strength or hardness, but these observations are not well established.

It is well known that the first effect of annealing cold-worked brass is a slight hardening. Bengough and Hudson, working with a 70:30 brass, found that the tensile strength increased in all cases with rise in annealing temperature up to about 300° C. The yield point remained practically constant up to 100° or higher, after which it dropped off. The effect of rest and low temperature annealing on the elastic limit was investigated in one case, and it was found that the elastic limit was not affected by aging for 12 days at ordinary temperatures or by heating for 1 hr. at 90° C. The yield point was raised by both

¹ Discussion on "Physical Properties of Nickel," by Browne and Thompson, *Trans. Am. Inst. Mining Eng.*, vol. 64, p. 414.

of these treatments. Annealing 1 hr. at 210°C . considerably decreased both elastic limit and yield point.

Bassett and Davis,¹ in their careful work on the relation of grain size to Brinell hardness in cartridge brass, found that annealing at low temperatures increased the Brinell hardness of the cold-worked metal, the increase being more marked the greater the reduction by rolling. This is shown in Fig 76.

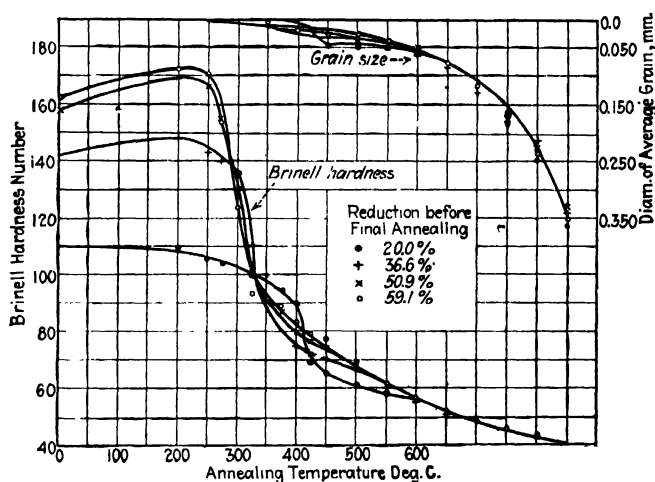


FIG. 76.—Effect of heating on Brinell hardness of cold-worked brass. (Bassett and Davis.)

The increase of tensile strength reported by Bengough and Hudson has been confirmed by Mathewson and Phillips.² Their material was a very pure 70:30 brass, which had been reduced cold 40 per cent. In this condition the average properties (five tests) were: tensile strength 76,763 lb. per square inch, elongation 11.1 per cent, and scleroscope hardness 33.2. After heating for $\frac{1}{2}$ hr. at 200°C ., the tensile strength (average of five tests) was 78,512, elongation 10.0, and hardness 34.2. Annealing at 300°C . caused appreciable softening and visible recrystallization.

¹ BASSETT and DAVIS, "A Comparison of Grain Size Measurements," *Trans. Am. Inst. Mining Eng.*, p. 428, vol. 60, 1919.

² MATHEWSON and PHILLIPS, "Recrystallization of Cold-worked Alpha Brass on Annealing," *Trans. Am. Inst. Mining Eng.*, vol. 54, p. 611, 1916.

In connection with their investigation of season cracking in brass, Moore and Beckinsale¹ have determined the effect of heating for 1 hr. at temperatures from 250 to 325° C. on the elastic limit. Their curves are reproduced in Fig. 77. It will be observed that the treatment at 250° C. practically doubled the proportional limit. Treatments at higher temperatures have in

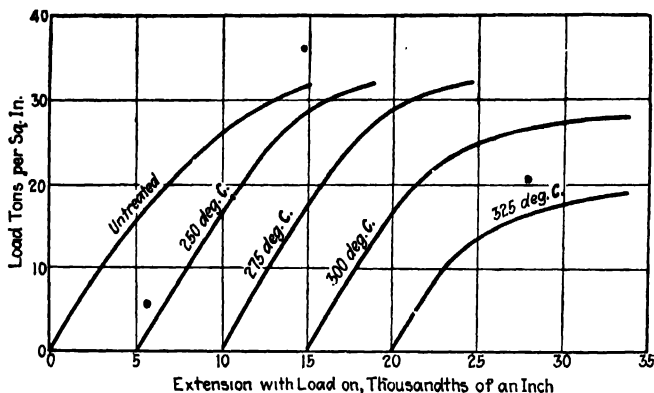


FIG. 77.—Effect of heating at low temperatures on elastic properties of cold-worked brass. (Moore and Beckinsale.)

all cases left the metal in an elastic condition, although the proportional limit decreases as the temperature of treatment is raised.

Hardening effects have been observed in nickel silver. F. C. Thompson found that the Brinell hardness was increased from 130 to 143 by annealing $\frac{1}{2}$ hr. at 300° C. Price and Davidson² have also reported an increase in both yield point and tensile strength on annealing cold-worked nickel silver at 350° C.

On the basis of the theory given above for the blue heat properties of iron, it might be expected that brass and nickel-silver would show discontinuities in hardness and strength when tested slightly above room temperature. Unfortunately, most of the work on the properties of these alloys at higher temperatures has not included tests between 20 and 200° C.

The evidence on the occurrence of overstrain and blue heat phenomena in metals other than iron is thus rather limited.

¹ MOORE, H. and BECKINSALE, S., "The Prevention of Season-cracking in Brass by the Removal of Internal Stress," *Trans. Faraday Soc.*, vol. 17 p. 162, 1921.

² PRICE and DAVIDSON, "Physical Tests on Sheet Nickel-Silver," *Trans. Am. Inst. Mining Eng.*, vol. 64, pp. 510-523.

There is a strong indication that the phenomena are of general occurrence, although they are certainly most prominent in iron. It may or may not be of some significance that both iron and nickel are magnetic and that the extent to which spontaneous hardening is manifested is greater in the more magnetic element.

Internal Stresses and Creep.—When a bar of iron is unloaded after being strained beyond its yield point, it does not return immediately, but approaches a stable position with increasing slowness. A more familiar example of the same phenomenon is found in the behavior of iron or steel when it is attempted to bend a piece to some desired shape, as in “straightening” a forging. It is at once apparent that, in order to make the piece assume a final desired position, it is necessary to bend it *past* this position, as there is an immediate elastic spring toward the original shape. Having caused the piece to assume the desired shape, it may be found some days later that it has returned still further toward its original shape. This slow return is often called *creep*.

Creep is due to the action of internal stresses, produced by the deformation, slowly moving the crystalline fragments back along the slip planes toward their original positions. As has been remarked before, the elastic limit of a piece of metal is not passed until stresses are set up in some of the grains exceeding their shearing strength along the planes of easy slip. By the time the yield point is reached, practically all of the crystalline metal is highly stressed. When the load is removed, these elastic stresses are, to a large extent, relieved, but some remain to be gradually lessened by the slow movement of the grain fragments along the slip planes. Freshly formed slip planes have a relatively low resistance to motion. After elastic recovery is complete, little or no creep is to be expected. As a practical example, steel forgings are often straightened at or above a blue heat, so as to “stay put.” The internal stresses set up by overstraining are never completely relieved unless the metal is in a semiplastic condition in which its elastic limit is substantially zero. That is, internal stresses are relieved only by flow, and their relief is opposed by elasticity. Metals and alloys which are elastic at ordinary temperatures are left in a state of internal stress (also spoken of as “internal strain”) by all commercial cold-working processes. High internal stresses can also be produced by uneven temperature changes. Rapid cooling, uneven sections, and mass contribute to such stresses.

The algebraic sum of the internal stresses in a piece of metal must always be zero; that is to say, tensile stresses in one portion are balanced by compressive stresses in other portions. An analogy may be drawn to the various members of a steel bridge, which may each be stressed in a different way, in tension, in compression, under bending, or under combinations of such stresses, although the entire structure is in a state of equilibrium as regards external forces. Now if a bridge member in tension is cut in two, its ends spring apart, and the sound members rearrange their loadings as best they can; on the other hand, if a compression member is cut, the ends come together. Internal stresses in a piece of metal can be detected and measured by means of the same principle.

If a light cut is machined from the surface of a piece of cold-drawn rod whose length has been carefully measured, a second measurement will show that the length of the remaining bar has increased. This means that, initially, the external layers of the rod were in a state of tension while the core was in compression. On removing some of the exterior metal, which was holding the core in compression, the compressive stress in the core is partly released and it automatically increases in length a corresponding amount. The average stress intensity in the layer of metal which has been removed can be calculated from the observed change in length of the remainder of the rod: the relative change in length, times the modulus of elasticity, gives the stress which has been released; this stress, multiplied by the area of the section, gives the total force released, which is exactly equal to the tensile force in the metal machined off. This force, divided by the cross-section area of the metal machined off, gives the average stress intensity in that metal.

The dimensional changes which result from cutting away part of an internally stressed piece of metal are often a source of considerable trouble. A surface originally machined "true" may be thrown out of true on removing stressed metal from some other portion of the piece.

If the external load to which a metal is subjected in service happens to be added to internal stresses already present in the piece, the total stress may exceed the strength of the material and failure may result at an external load far below that which would normally cause failure. Under some exceptional circumstances, it is possible to utilize internal stresses to oppose

external loads and thus extend the useful strength of the metal. Ordinarily, however, internal stresses are considered to be a source of weakness.

Metals sometimes fail spontaneously from internal stresses. The most common examples are hardened steel and cold-worked brass. Severe stresses are set up in steel by the hardening operation, both by uneven temperature changes in themselves and by the volume changes incident to hardening and aging. Such induced stresses are often sufficient to burst the steel, either during the hardening or some time thereafter.

Removal of Internal Stress in Brass.—Cold-worked articles of brass, such as cold-drawn bars, cartridge cases, or spun jars or cups, often split open spontaneously. The failure may occur months or years after fabrication, and is known as "season cracking." It is due to internal stresses induced by cold working, assisted usually by corrosive action. Season cracking can be prevented by so controlling the deforming operations as to avoid setting up excessive internal stresses or by reducing the internal stresses to a safe value by annealing. It was shown by Merica¹ that the internal stresses in brass can be reduced below the danger point by annealing at temperatures too low to produce visible recrystallization or appreciable softening. More recently a very interesting quantitative study of the removal of stresses in brass by low temperature annealing has been reported by Moore and Beckinsale.² Their results are summarized as follows:

1. The rate of reduction of stress is fairly rapid at 200° C. at first, but becomes very slow when the stress has been reduced to one-half to one-third its initial value and important stresses remain even after treatment for 24 hr. or longer.

2. As the temperature is raised the rate of reduction of stress increases, but shows the same characteristic of slowing down as the stress falls. At 300° C. a very much shorter time is required to reduce the stress to a given figure than at 200° C. and the remaining stress is much lower after a given time at the higher temperature, in brass of the same hardness.

3. The higher the initial stress the higher is the remaining stress after a given treatment, in brass of the same hardness, although the amount of stress removed is greater the higher the initial stress.

4. The higher the hardness of the brass the lower is the remaining stress after a given treatment and for a given initial stress. In other

¹ MERICA, P. D. and WOODWARD, R. W., "The Failure of Structural Brasses. *Trans. Am. Inst. Metals*, vol. 9, p. 298, 1915.

² See note 1, page 191.

words, the harder the brass the more rapidly is a given initial stress reduced at a given temperature.

5. A large reduction in the amount of stress is brought about by annealing conditions (temperature and time) which raise the hardness of cold-worked 70:30 brass, but treatments which result in some reduction of hardness are necessary to bring about complete removal of stress.

6. At temperatures in the range 200 to 300° C. slight plastic flow occurs in cold-worked brass at low stresses. The amount of flow is greater as the temperature is higher, the stress greater and the time longer for which the stress is maintained.

7. The reduction of internal stress by low-temperature annealing is dependent on the plastic flow mentioned in (6).

8. This plastic flow involves a lowering of the elastic limit at the temperature at which it occurs. This reduction of elastic limit is, however, not permanent, provided the treatment is applied for a time not exceeding 1 hr. at 275° C. or certain limiting times which are much longer at lower temperatures. The limit of proportionality and elastic limit are raised considerably by treatments which do not exceed these limits of temperature and time.

These results are true specifically only for a 70:30 brass, but some general conclusions are warranted regarding the removal from other metals of internal stresses induced by cold work or temperature changes. The temperatures at which stresses are removed from brass are near the lowest temperature of recrystallization. Complete removal of stress required an annealing which produced some softening and hence some recrystallization. It is probable that any metal must be heated to a temperature near its recrystallization temperature to remove stresses; heating to higher temperatures will result in more complete removal.

Hardening by Cold Work.—Most metals are hardened by working at ordinary temperatures. Tin and lead anneal rather quickly, so that a quick test is required to detect much hardening. Zinc also anneals at room temperature, but more slowly, so that considerable temporary hardening can be produced. The tensile strength of the ordinary metals, like iron, copper, and aluminum, is increased from two to three times by commercial cold-working processes. The plasticity of a metal has probably never been exhausted by cold working, since, with sufficient care, an almost unlimited amount of work may be carried out. Copper can be cold rolled from a slab $1\frac{1}{2}$ in. thick to a sheet having a thickness of 0.002 in. Copper can also be easily cold drawn until its length has been increased 5,000 times. Tungsten has

been extended 200,000 times in length by working below its recrystallization temperature. By this it is not to be understood that extremely high reductions by cold working are always practicable or desirable, but merely that they are sometimes possible.

While the general effects of cold working are an increase in hardness and loss of plasticity, various specific properties are affected in somewhat different ways. As noted above, when discussing overstrain, the elastic limit of iron is lowered sometimes to zero by cold working, but is restored by aging or heating at low temperatures to a value which may be much higher than its original value.* It has also been shown that the elastic limit of cold-worked brass may be raised from 22,400 to 44,800 lb. per square inch by low temperature heating. There is a lack of exact information regarding the effect of cold working and aging on the elastic properties of other metals.¹ Beilby¹ tested the elasticity of metals by making reed vibrators of them and observing the pitch and intensity of the notes produced. He found that cold-worked copper, silver, and gold gave notes of greater intensity (*i.e.*, had a greater amplitude of vibration), but lower pitch (lower frequency of vibration) than when annealed. This indicates that the cold-worked metals are less perfectly elastic than the annealed metals or have a slightly lower modulus of elasticity, but that they are elastic or nearly so up to much higher stresses.

The yield point is probably affected by cold working more than any other property of the hardness group. While the tensile strength of iron (in wire) is raised from 48,000 to 125,000 lb. per square inch, the yield point is raised from about 25,000 lb. per square inch up to a value practically identical with the tensile strength. Similar results are obtained with other metals, the ratio of yield point to tensile strength increasing markedly as cold working progresses.

Figures are often given, particularly in handbooks, indicating that the elastic modulus is greater in the cold-worked than in the annealed condition. Such results are reported especially for the softer metals and alloys like copper and brass, whose true elastic limits are quite low when in the annealed condition. The

¹ BEILBY, G. T., "The Hard and Soft States in Metals," *J. Inst. Metals*, 1911, No. II, p. 5. For a complete account of Beilby's work see his more recent book, "Aggregation and Flow in Solids," Macmillan, 1921.

lower moduli reported for the annealed metals were probably calculated from stresses which exceeded the true elastic limit. If there is any real difference in modulus, that of the annealed metal is probably the greater.

The hardening effect of cold work is indicated to somewhat different degrees by the various tests for hardness. The scleroscope shows the greatest effect followed by the Brinell test.

Resistance to repeated stresses is increased by cold working. This is particularly noticeable in the softer metals, which can be used for springs when cold worked, a service for which they are entirely unsuited when in the annealed condition.

The effects of cold working are directional.¹ The increase in elastic limit and yield point are greatest in the direction of working, and there may even be a decrease in elastic limit under forces applied in the opposite direction. Cold-rolled or cold-drawn metals are generally used in such a way that the service stresses are in the same direction as the working stresses.

Elongation is reduced by cold working. After very severe working the elongation before rupture is almost entirely elastic. The per cent reduction of area is also decreased by cold working, but to a less marked extent than is the elongation. The reduction of area of a cold-worked metal may even be greater than that of annealed metal of large grain size. For example, a copper rod reduced by cold swaging from 0.5- to 0.10-in. diameter had a rather high reduction of area. After annealing at 700° C., the reduction of area was somewhat less.

The hardening effect of a small or moderate deformation is greater the smaller the grain size of the metal subjected to such deformation. The strength obtainable by severe cold working is about the same regardless of the initial grain size, so that a coarse-grained metal which originally has a lower strength than a fine-grained metal must be regarded as possessing greater capacity for hardening by cold work.

In general, the increase in hardness and loss in plasticity are continuous with increasing amounts of cold work. The rate of change tends to decrease as the amount of work becomes large.

For instance, a discontinuity in the effect of cold work on the properties of copper has been reported by Alkins.² He found

¹ VAN DEN BROEK, J. A., "The Effects of Cold Working on the Elastic Properties of Steel," *Carnegie Scholarship Memoirs, Iron Steel Inst.*, vol. 9; also see *Engineering*, July, 1918.

² ALKINS, W. E., "The Effect of Progressive Cold Work upon the Tensile Properties of Pure Copper," *J. Inst. Metals*, No. II, vol. 20, p. 33, 1918.

that when copper was reduced by wire drawing, a stage was reached at which a reduction of area of almost 10 per cent was accompanied by no change in tensile strength. This occurred when the diameter had been reduced from 0.553 to 0.373 in. in four successive passes. The tensile strength at this stage was about 52,000 lb. per square inch. He also reported that wires which had been reduced less than this amount and which had a tensile strength less than 52,000 lb. per square inch were stable at ordinary temperatures, whereas wires which had been reduced a greater amount and which shortly after drawing possessed higher tensile strength were in an unstable condition and underwent a gradual reduction in strength at ordinary temperatures. The interruption in the hardening process on continued cold drawing is probably attributable to spontaneous annealing.

After a metal has been severely cold worked, further cold working may cause a decrease in tensile strength. This is the result obtained when wires are "overdrawn." It is usually due to internal failures, such as splitting or drawing hollow. Strength normally increases as cold working progresses, as long as complete continuity of the metal is maintained. If the temperature of working is sufficiently close to the temperature of recrystallization, severe working may cause some annealing.

Commercial Terms for Hardened Metal.—Commercially, metals are supplied in various degrees of hardness according to the purposes for which they are to be used. The various grades are designated by such terms as soft or annealed, medium or half hard, and hard. A specially hard grade of brass is denoted by the term "spring temper." Aluminum sheet is supplied in various tempers designated by numbers which indicate the amount of reduction by cold rolling subsequent to annealing. When it is desired to produce a finished article by some cold-working operation, such as spinning or pressing, and to have a certain degree of hardness in this finished article, sheet is selected of such temper that, when subjected to the further deformation of the fabricating process, it will have the desired final hardness.

The amount of cold working which is necessary to produce material of any particular hardness is different for different metals. Copper wire is obtained in the half-hard condition by a reduction in section of about 60 per cent. A reduction in section of about 90 per cent is required to produce hard wire. These fig-

ures are typical of a pure metal of great plasticity. Less plastic metals and alloys, such as brass, harden more rapidly.

In general, the hardening effect of a given deformation is greater the lower the temperature at which deformation is effected. This is illustrated by some tests reported by Beilby.¹ Some gold wire was drawn at room temperature so that its length increased from 186 to 352 mm. It was then drawn part way through a final die at room temperature, the remainder of the wire being drawn through the die at a temperature of approximately -80°C . In this final pass, the length of the wire was increased 32 mm., making the total length 384 mm.; therefore the total extension of the wire from the soft condition was then 106 per cent.

The tensile strength of the wire which had been drawn entirely at room temperature was 32,368 lb. per square inch, whereas the tensile strength of the wire which was finished at -80°C . was 35,213 lb. per square inch. The wire drawn at the low temperature was thus 8.8 per cent stronger than the wire drawn completely at room temperature. Some copper wire treated in the same way showed a tensile strength of 60,928 lb. per square inch for the wire drawn entirely at room temperature and 64,960 for the part finished at -80° , an increase of 6.6 per cent.

The fact that iron is hardened much more by working in the blue heat range than at certain lower temperatures has been referred to, and it has been indicated that this behavior may be a general property of metals, although it is found to an exceptional extent in iron.

With the exception of tungsten and molybdenum, metals are usually worked either above their recrystallization temperatures or at room temperature—that is to say, intermediate temperatures are not intentionally selected for working and probably in no case is an artificially low temperature intentionally used. Work is often applied at temperatures between the recrystallization temperature and room temperature, however, in the natural sequence of operations. Thus ingots of copper or aluminum may be started through the rolls hot—that is, above the temperature of recrystallization—and rolling may be continued while the metal cools down gradually to room temperature. On the other hand, the heat produced by cold deformation itself may

¹ See note 1, page 196.

raise the temperature of a metal somewhat above the assumed working temperature. It has been estimated that in drawing copper wire presumably at a temperature of about 20°C . the actual temperature may be about 75°C .

Variations in the conditions of cold working are unlimited in respect to such factors as the stages of reduction, the speed of drawing or rolling, and the shape of dies or rolls. Variations in such factors produce slight variations in the properties of the metals, because of uneven distribution of the deformation, or of temperature and time effects. For practical purposes, however, the properties of a cold-worked metal are nearly independent of the manner of deformation.

Cold-worked Metal at Elevated Temperatures.—The properties of cold-worked metals vary with temperature in much the same way as do their properties in the annealed condition. Hardness decreases with rising temperature. Tensile strength decreases with rising temperature throughout the intermediate zone of temperature, but also decreases on cooling into the low-temperature region of brittleness. Thus cold-drawn tungsten wire—like annealed tungsten wire—is weaker at liquid air temperature than at room temperature. No other metal so far tested is weaker at the temperature of liquid air (-185°C .) than at room temperature, but most metals probably become weaker at some temperature lower still.

The elongation of cold-drawn wires likewise follows the same general trend as that of annealed wires. As the temperature rises from the cold brittle region, the elongation increases to a maximum value, and then, on further rise of temperature, decreases. The temperature of maximum elongation, however, is lower for cold-worked metal than for annealed metal, at least for those metals whose loss of ductility at low temperatures is due to grain boundary brittleness. It is in accordance with this law that cold-drawn tungsten wire is ductile at room temperature, whereas recrystallized tungsten wire is brittle. At temperatures above that of recrystallization, the effects of cold working are lost, and the properties become those of annealed metal, depending upon the grain size established by the conditions of deformation and heating.

When there is a discontinuity in the effect of temperature on the mechanical properties of a metal in the annealed condition, a corresponding discontinuity is found in the properties of the

cold-worked metal. For example, the blue heat properties of annealed iron are also found in cold-worked iron, but are less evident as the amount of cold working increases.

Cold-worked metals are nearly completely annealed or softened by heating under conditions of time and temperature that produce general visible recrystallization. Some softening may occur at much lower temperatures. It has already been mentioned that iron which has been severely cold worked and aged is softened somewhat by heating at 100° C., although visible recrystallization occurs only above 450° C., and that hard copper wire loses some of its strength slowly at room temperature. It has also come to the authors' attention that springs which depend for their elasticity on hardness produced by cold work gradually deteriorate to some extent at ordinary temperatures so that they become unfit for certain uses.

Summary of Properties.—The following general statements may be made regarding the properties of cold-worked metals:

1. Hardness and strength of a metal increase with the amount of reduction by cold work until internal failure is produced.

2. Plasticity of a metal decreases as the amount of cold work increases.

3. With change in temperature of test, the properties of a cold-worked metal follow those of annealed metal, any discontinuities in the properties of annealed metal being reflected in those of cold-worked metal.

4. The effect of a given deformation is greater the lower the temperature at which it is effected, except that in some metals abnormally large effects are produced in a certain region of temperature, for example the blue heat range in iron.

5. Elongation of a cold-worked metal increases with respect to the elongation of annealed metal, as the temperature of test decreases below the working temperature, reaching a maximum value, after which further decrease in temperature produces a rapid decrease in elongation.

6. Elongation of a cold-worked metal decreases with respect to the elongation of annealed metal as the temperature of test is raised above the working temperature, until the recrystallization temperature is reached, when elongation is increased by annealing.

7. Temperatures of maximum elongation are different for various metals.

8. For any given metal, the temperature of maximum elongation is lower the greater the amount of cold work, and is, in general, lower in cold-worked metal than in annealed metal.

9. In metals which become brittle on cooling because of intercrystalline weakness, the cold-worked metal may possess considerable elongation at temperatures at which the equiaxed metal is brittle.

10. The greater the amount of cold work the less is the elongation at the temperature of working or at the temperature of maximum elongation on cooling.

11. The hardening effects of slight or moderate deformations are greater the smaller the initial grain size of the metal.

12. Reduction of area of a cold-worked metal is, in general, less than in the annealed state.

Conditions at Slip Planes.—The properties of cold-worked metals and the phenomena of plastic deformation indicate that important changes may take place on the surfaces of slip during and after deformation. A number of propositions regarding the conditions at slip planes are herewith presented. For the purposes of this discussion, the term "slip plane strength" will be used to denote the resistance to motion along a slip plane after slip has started. "Crystal strength" means the shearing strength of the unbroken crystal on planes parallel to the slip plane under consideration; it is the resistance to motion on the slip plane, *before* slip starts.

1. *Immediately after slip begins, the slip plane strength is less than the crystal strength.* In coarse-grained metals, slips are readily observed which have extended for a distance of several thousand atom diameters. In single crystals tested in tension, the extent of the motion on individual slip planes is still greater. After slip has once started, therefore, the resistance to further motion on the same plane must, for a while, be less than the resistance to the starting of slip on a parallel plane and hence less than the original shearing strength of the crystal. When iron has been recently overstrained, the application of very small stresses results in permanent deformation which must take place by motion on the slip planes formed in the first overstraining process. Resistance to motion on these planes must, therefore, be quite low as compared with their original strength. The same is true of brass or other metals whose elastic limit is decreased by overstraining.

2. As slip continues, the slip plane strength increases to a value which may be greater than the crystal strength. It is a striking fact that, when single ductile crystals are tested in tension, failure does not occur on the first slip plane. Motion continues for a certain distance, after which further deformation takes place by slip on other planes. This means that the resistance to motion on the original slip plane must have increased to a value somewhat greater than the resistance to motion on parallel planes in the crystal. The process of slip may be termed "self-stopping."

3. In a metal composed of an aggregate of grains, slip is stopped partly by the interference of adjacent grains and partly by the resistance on the slip plane itself. In a single crystal, which is ductile it is necessary that motion continue on the first slip plane until the resistance to motion automatically becomes greater than that in the unbroken crystal. In an aggregate composed of many grains, however, motion on a slip plane in any one grain is opposed by adjacent grains through which there are no corresponding planes of weakness. Slip may there be brought to a halt by end resistance before sufficient motion has taken place to increase the resistance on the plane to the self-stopping point.

4. Slip planes in all stages of their history are present in cold-worked metals. Since the slip plane strength increases with motion along the plane and since the extent of the motion on the various slip planes is different according to the various conditions of external support, it is evident that the resistance to motion on the various slip planes after deformation stops may be anything from the minimum to the maximum obtainable.

5. Slip causes rupture of the atomic bonds on the slip plane, and immediately after motion has stopped there is only partial reestablishment of cohesion.

6. When the registry of the displaced crystal fragments permits, cohesion is reestablished by the fragments joining into larger crystal-line units. The slip plane then disappears as such, being replaced by a potential slip plane whose strength is equal to the crystal strength.

7. As a rule, the crystal fragments do not register after deformation, and all degrees of disregistry occur. It has been shown by x-ray analysis that new orientations are created by plastic deformation. Consequently, there must be many, probably a large majority, of crystal fragments whose orientations do not permit them to unite except by the process of grain growth.

8. *Reestablishment of cohesion between crystal fragments of different orientations must be attended with various degrees of disorganization as regards the arrangement of the atoms at the slip plane.*

9. *This metal of partly disorganized structure simulates an amorphous material in its mechanical properties.* The characteristic properties of typical amorphous materials are, first, the great influence of time upon deformation, and, second, the rapid change in properties with change in temperature. Cold-worked metals behave as though the resistance to motion on the slip planes varies in a similar manner with time and temperature. The slip plane strength increases on cooling and decreases on heating at a more rapid rate than does the crystal strength. For example, the tensile strength of cold-worked iron increases on cooling much more rapidly than the tensile strength of annealed iron.

10. *Atomic rearrangement on slip planes takes place at temperatures much lower than are usually associated with recrystallization.* During the spontaneous aging of overstrained iron at ordinary temperature, or the rapid recovery of elasticity at a blue heat, the slip plane strength increases so that small stresses no longer produce permanent deformations. This increase in slip plane strength, or "healing," as it may be called, may consist in the growing together of fragments of sufficiently similar orientation, or in the establishment of cohesion at additional places on the planes between fragments that do not register. Rosenhain has observed that, when a piece of iron is polished immediately after overstrain, lines are found which probably represent the intersection of the polished plane of the specimen with the surfaces of slip. These lines (called α -bands by Howe) are not found in the specimen if permitted to rest or recover before polishing. Lea has reported that the recovery of iron or mild steel from overstrain is accompanied by an *increase* in density. All evidence is to the effect that the healing process involves an increase in the continuity of the metal. Although the electrical conductivity of metals is decreased by cold working and is, in general, least when the metal is in its hardest condition, it is to be expected that the hardening of a cold-worked metal like iron by aging or heating at low temperatures would be accompanied by an *increase* in conductivity. Further heating would produce a continued increase in conductivity but eventually a decrease in hardness.

11. *At certain temperatures slip planes may heal during deformation.* This is what happens at a blue heat in iron and at similar temperatures in nickel. When the slip plane strength exceeds the crystal strength, deformation is forced to take place on new slip planes. Spontaneous healing during deformation therefore results in a more intricate system of internal deformation.

12. *On lowering the temperature, the slip plane strength may increase to a value greater than the crystal strength without any healing taking place.* For a given degree of disorganization at the slip plane and a given degree of reestablishment of cohesion, the ratio of slip plane strength to crystal strength is greater the lower the temperature. Slip may, therefore, reach a self-stopping state at low temperatures after less motion than at higher temperatures. This would lead to greater internal working by a given external deformation at low temperatures than at high temperatures. This excess of slip plane strength over crystal strength at low temperatures is the fundamental cause of the general increase in elongation with decrease in temperature of test, and, in particular, of the fact that wires drawn at certain temperatures until their ductility is nearly exhausted regain ductility on cooling to lower temperatures. Elongation takes place after the yield point is passed. Yield point is a function largely of crystal strength, being the stress required to deform the crystal. After the yield point is passed, permanent deformation of the metal continues as long as the strength is sufficient to sustain the deforming load. Rupture finally takes place at the slip planes. An increase in slip plane strength as compared with crystal strength therefore raises the tensile strength as compared with the yield point, and hence promotes elongation before rupture.

13. *The properties of the disorganized metal at the slip planes probably never become those of the hypothetical vitreous amorphous metal which would prevent any further motion on the same planes during further plastic deformation.* This has been discussed more fully in Chap. IV, in which it was pointed out that slip planes must be used repeatedly to account for the large amounts of plastic deformation that are possible.

Cause of Strain Hardening.—It has been mentioned before that a strain-hardened metal is unique in properties and structure. The structure is unique because the shapes of the grain fragments are largely determined by crystallographic planes, and,

on account of the manner of origin of the structure, there may be only a very slight disregistry of slip planes from grain fragment to grain fragment.

It has been found by *x*-ray crystal analysis¹ that the first mechanical working of coarse-grained metals produces mixed

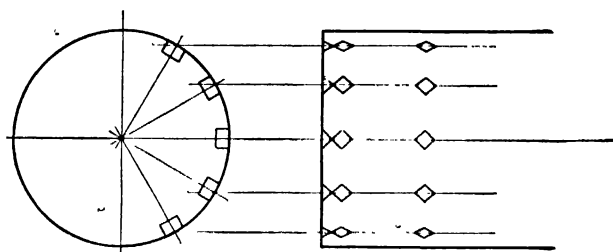


FIG. 78.—Preferred orientation of crystal fragments in severely drawn wire of metal crystallizing with body-centered cubic space lattice.

orientations of the crystal fragments within the large grains. The mixing may not be, and perhaps is never, sufficient to produce random orientation of the crystal fragments within a single original grain.

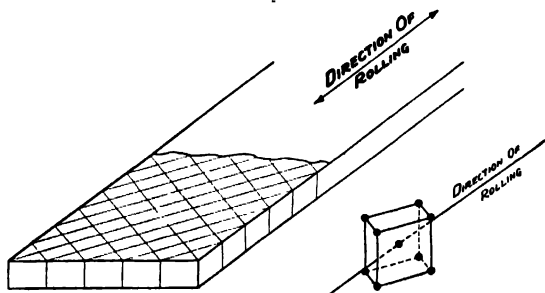


FIG. 79.—Preferred orientation of crystal fragments in severely rolled sheet or foil of metal crystallizing with body-centered cubic space lattice.

It has also been shown by *x*-ray crystal analysis that severe cold working tends to orient the crystal fragments in certain definite directions with reference to the direction of working.²

The preferred orientation of the crystal fragments in a severely drawn wire of a metal crystallizing with a body-centered cubic space lattice is shown in Fig. 78. One of the cube faces (100) is

¹ BAIN and JEFFRIES, *Chem. Met. Eng.*, p. 775, Oct. 26, 1921.

² BURGER, *Physica*, vol. 1, p. 214, 1921; POLANYI and WEISENBERG, *Z. Tech. Physik.*, vol. 4, p. 199, Nov. 30, 1923; JEFFRIES, Institute of Metals, Div. of Am. Inst. Mining Eng., February lecture, 1924.

parallel to the surface of the wire at any point, and the other two cube faces are perpendicular to the surface of the wire and make angles of 45 deg. with the direction of working. Figure 79 shows the preferred orientation in severely cold-worked sheet or foil of a metal crystallizing with a body-centered cubic space lattice. One of the cube faces (100) is parallel to the surface of the sheet or foil and the other two cube faces are perpendicular to the surface and make angles of 45 deg. with the direction of working.

In the working of a metal composed of a large number of randomly oriented grains, the tendency is for the crystal fragments produced by the intersecting systems of slip planes to assume the same ultimate orientation, regardless of the initial orientation. In a given grain, the change of the various crystal fragments toward the preferred orientation will not be simultaneous. Furthermore, not all of the grain fragments ever attain the preferred orientation exactly, even in the most severe cases of cold working.

A cold-worked metal, therefore, consists of grain fragments very much smaller than any grains found in a recrystallized metal. Owing to the very slight difference in orientation from grain fragment to grain fragment in cold-worked metal, the properties are not the same as if each grain fragment consisted of an individual grain with marked difference in orientation between adjacent grains. Even the preferred orientation in severely worked metals favors a high reduction of area in specimens broken in tension.

The authors prefer to consider the structure of cold-worked metals as simulating a fine-grained structure but not wholly equivalent to a very fine-grained structure.

The movement of crystal fragments on a number of intersecting systems of slip planes gradually destroys continuity of the planes of weakness in proportion to the degree of disregistry at boundaries between grain fragments. Since the resistance to motion along the slip plane may be greater than in the unbroken crystal, such slip planes are sources of strength and hardness aside from the slip interference action. In this respect it may be said that the creation of disorganized structures whose properties simulate those of an amorphous material is a cause of hardness in cold-worked metals. However, the importance of such amorphous metal in hardening seems to have been greatly exaggerated. Strain hardness is, therefore, to be attributed

chiefly to the slip interference created by the new positions of the crystal fragments. The hardening is greater, in general, the larger the number of planes on which slip takes place. A given external deformation will therefore produce greater hardness the greater the number of slip planes produced or the greater the internal working of the metal. In accordance with this principle, deformation produces hardness more rapidly as the temperature is lowered, and as the initial grain size is smaller, and, finally, when spontaneous healing takes place during deformation (as in the blue heat range in iron).

Tammann developed a theory of strain hardening based on the proposition that movement at slip planes was entirely one of translation, that is, all the crystal fragments formed within an original grain are supposed to retain the initial orientation of the original grain. He postulated that strain hardness was due to the different degrees of hardness of the crystal in different directions, there being a direction of minimum hardness and a direction of maximum hardness. In the first stages of deformation, slip was supposed to take place largely in those grains of such orientation that the planes of easiest slip made angles of about 45 deg. with the direction of the load. With each successive increase in load, it would be possible for slip to take place on planes in less favorable angles for slip. This is supposed to be the mechanism for increase in yield point or elastic limit as cold working progresses.

This theory is based on a wrong premise. It had not been proved that cold work produces crystal fragments of many orientations within an original grain. Tammann's theory also did not take into sufficient account the fact that in an aggregate of grains there must be simultaneous motion on slip planes of many grains during deformation. In fact, it is not possible to deform one grain in the interior of a piece of metal composed of a large number of grains without at the same time causing slip to take place in some or all of the adjacent grains.

The original grain boundaries persist after very severe cold working. It has been mentioned that the grain boundary surface increases as the grains are elongated, and it is suggested that additional amorphous metal is generated at the old grain boundary during deformation. This additional amorphous metal may have a hardening effect. Aside from this, the original grain boundaries in severely cold-worked metals may have a

pronounced effect on the tensile properties, especially in a transverse test. These grain boundaries have somewhat the effect of fibers of foreign material in certain cases. The causes of strain hardening may be summed up briefly as follows:

1. Cold work produces a structure which simulates in many respects that of a very fine-grained metal.

2. Because of the manner of origin of the cold-worked structure, each grain fragment may have an orientation only slightly different from that of its neighbors, so that a large number of grain fragments may be so oriented as to be traversed by a single slip. Slip through such grain fragments is, however, interfered with by the disregistry at the fragment boundaries, and therefore the hardness is increased. In other words, the main cause of strain hardening is the slip interference resulting from the disregistry of slip planes at the boundaries of grain fragments.

3. An additional cause of strain hardening is the disorganized layer of atoms at self-stopping slip planes and the additional amorphous metal generated at the old grain boundaries.

4. Since severe cold work tends to produce uniformity of orientation among the grain fragments, it is probable that there is a limit to the hardness attainable by cold work. Judging from the hardness of severely cold-worked iron and severely cold-worked aluminum, the maximum hardness attainable by cold work is much lower than that attainable by other methods, such as alloying and heat treating, and hence much lower than the hardness corresponding to the absolute cohesion of the metal.

Some Typical Examples.—The examples to be given include metals crystallizing with face-centered and body-centered cubic lattices. No extensive investigations have been reported on metals crystallizing with hexagonal lattices, but such information as is available indicates a tendency toward less plasticity, a narrower range of temperature within which they are plastic, and a tendency toward greater brittleness of the individual crystals than in cubic metals. The mechanical properties of the hexagonal metals are, however, in harmony with the general rules put forth here.

The data from which the accompanying curves were plotted are the results of tests made on wire of 0.025 in. diameter. In each case the elongation was measured on a length of 2 in. Testing conditions were similar for the various metals. For testing at low temperatures, a bath of liquid air was used; for tests at

100° C., boiling water; and at slightly higher temperatures, a bath of oil. At still higher temperatures, specimens were heated in an electric tube furnace, an atmosphere of argon being used to

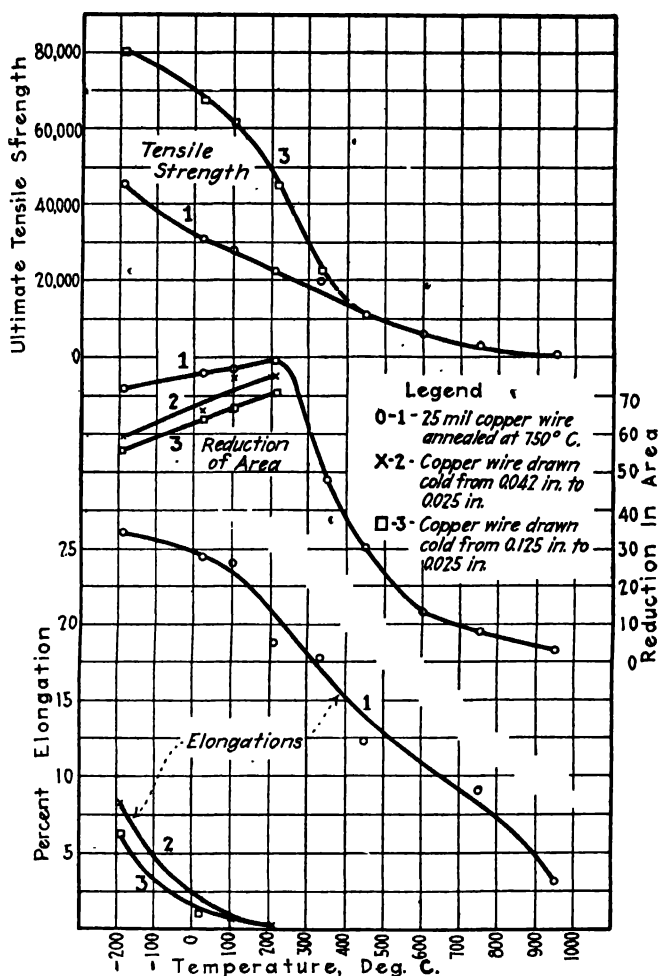


FIG. 80.-Effect of temperature on the tensile strength, elongation, and reduction of area of annealed and cold-drawn copper wires.

protect the specimens from oxidation when this was necessary. No determinations were made of elastic limit or yield point.

In Fig. 80 are two curves showing the variation in the tensile strength of annealed and cold-drawn copper with changing temperature. The curve for the cold-drawn wire is discontinued

above $330^{\circ}\text{C}.$, because in this range of temperature the wire anneals rapidly and becomes practically identical with the material represented in the other curve. Below the recrystallization temperature the strength of the cold-worked wire increases more rapidly than the strength of the annealed wire.

Figure 80 also shows the effect of temperature on the elongation of annealed copper wire and of two samples of cold-drawn wire reduced different amounts by drawing. Again, the elongation of

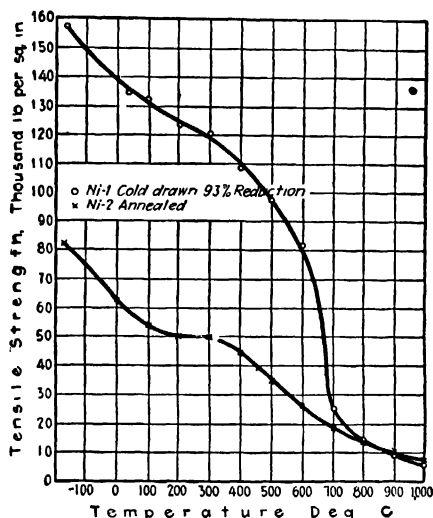


FIG. 81.—Effect of temperature on the tensile strength of cold-worked and annealed nickel wires. (Sykes.)

the cold-worked metal varies with temperature in the same manner as that of the annealed metal. At the lower temperatures the elongation of the cold-drawn wire increases more rapidly than that of the annealed wire, and the indications are that at some very low temperature the elongation of the cold-drawn wire might be the greater. Results are not plotted for temperatures above $200^{\circ}\text{C}.$ for the cold-drawn wires. Annealed and cold-drawn copper wires are also compared as to reduction of area in Fig. 80. The effect of temperature on this property is seen to be in the same general direction for cold-drawn and annealed wires. Again, results are not plotted above the recrystallization temperature.

Figure 81 shows the effect of temperature on the tensile strength of annealed and cold-drawn nickel wire and records the same

general tendency of decrease in strength with increase in temperature noted for copper. There is a marked break in the curve at 200 to 300° C. for the annealed wire. This has been discussed above and is believed to be due to spontaneous healing of slip planes during deformation. The same discontinuity is reflected in the curve for the cold-drawn wire, but is less apparent. Annealing is seen to take place rapidly at 600 to 800° C.

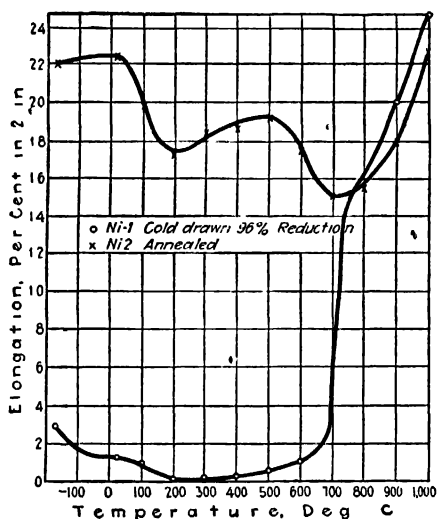


Fig. 82.—Effect of temperature on the elongation of cold-worked and annealed nickel wires. (Sykes.)

Elongation-temperature curves for the same nickel wires are shown in Fig. 82. Below the temperature of recrystallization, annealed wire appears to have a general tendency toward increased elongation with decreasing temperature. This general trend is broken at 200 to 400°, the minimum in elongation at 200° C. corresponding with the horizontal portion in the tensile strength curve. A slight drop in elongation on cooling from room temperature to the temperature of liquid air is probably due to the beginning of low-temperature brittleness. No tests were made between room temperature and liquid air temperature, and it is quite likely that at some intermediate temperature the elongation would be higher than at any point shown on the curve. Elongation of cold-drawn wire increases continuously as it is cooled from 200° C. down to the temperature of liquid air. The

fact that no drop in elongation at low temperatures is shown corresponds with the general observation that cold-drawn metals remain ductile at lower temperatures than annealed metals. The rise in elongation in the cold-drawn wire above 400° C. is due to annealing.

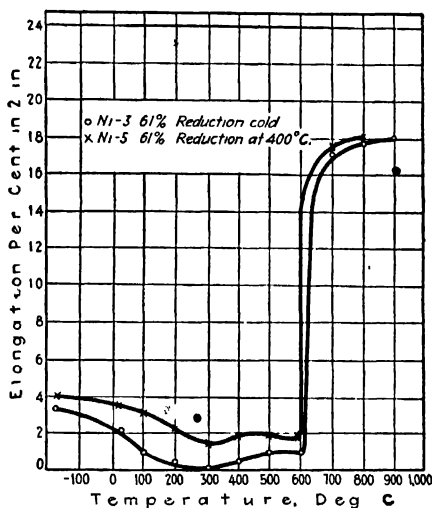


FIG. 83.—Effect of temperature on the elongation of nickel wires drawn at different temperatures. (Sykes.)

Figure 83 shows elongation-temperature curves for nickel wires reduced the same amount at room temperature and at 400° C. respectively. It will be noted that the elongation of the latter is higher, in accordance with the general rule that the effect of cold work is greater the lower the temperature at which it is effected. These wires, which have been reduced less than the one represented in Fig. 82, show distinct minima in elongation at 300° C., corresponding to the horizontal in the tensile strength curve for annealed nickel. In view of these curves, it is probable that the minimum in elongation shown in Fig. 82 is also at least partly attributable to this blue heat phenomenon.

Figure 84 shows the effect of temperature on the tensile strength of annealed and cold-drawn Armco iron wire. The strength increases with the amount of reduction by cold drawing. There is a general decrease in tensile strength with increasing temperature, but annealed wire shows a very marked increase in

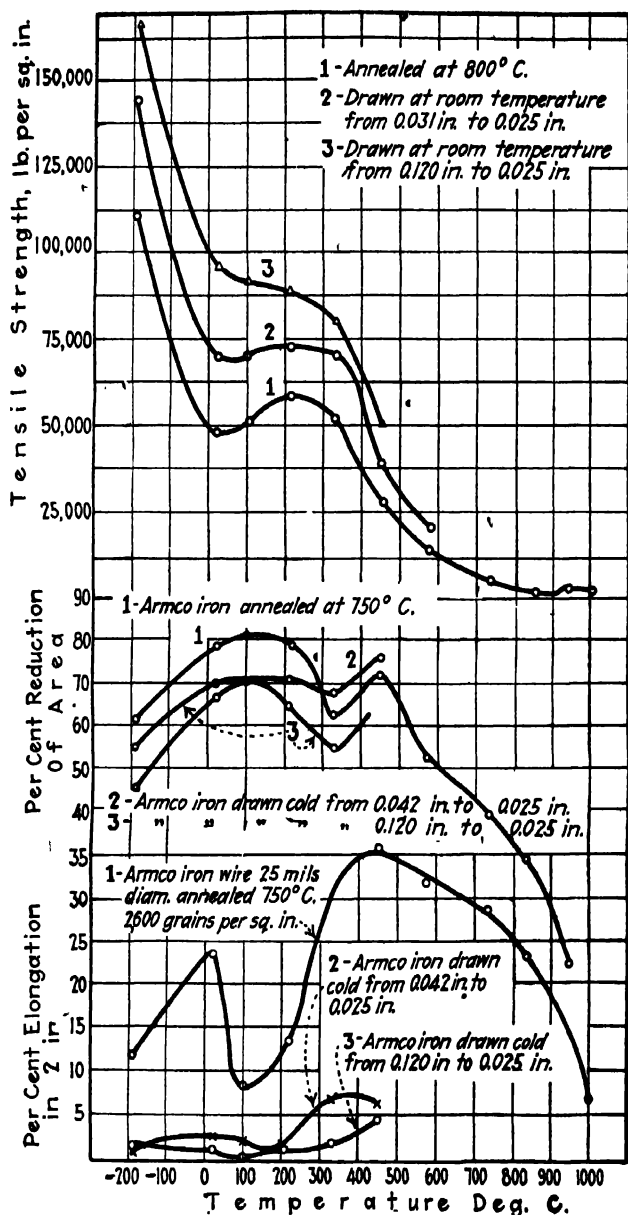


FIG. 84.—Effect of temperature on the tensile strength, elongation, and reduction of area of annealed and cold-drawn Armco iron wires.

strength on rising temperature, the strength reaching a maximum at about 200° C. As pointed out above, the actual temperature of this maximum depends quite largely on the rate of testing. The same discontinuity is shown in the cold-drawn wires, but to a less marked extent. There is also a considerable increase in strength on raising the temperature of annealed wire between 850 and 930° C., due to the allotropic change from Alpha to Gamma iron.

Elongation-temperature curves for annealed and cold-drawn iron wire are also shown in Fig. 84. Decrease in elongation of annealed wire at temperatures from 450° C. upward is in accordance with the general law. A marked minimum in elongation at 100° C. is due to the blue heat phenomenon. Below this temperature the elongation again rises in accordance with the general law to a maximum (which may be somewhat below room temperature), after which it decreases because of low-temperature brittleness. The cold-drawn wires also reflect the minimum in elongation in the blue heat range. Above about 450° C., annealing takes place, after which the properties become similar to those of the annealed iron. There is no positive evidence here that the elongation of the cold-drawn wires would be greater than that of the annealed wire at very low temperatures, but such may be the case.

The same figure shows the effect of temperature on the reduction of area of annealed and cold-drawn iron wire. The general tendency is as usual—a rise in reduction of area with increasing temperature up to the recrystallization temperature, above which the reduction of area decreases. The minimum in reduction of area at about 330° C. is again a manifestation of the blue heat phenomenon. It will be observed that the minima of elongation do not occur at the same temperatures nor at the same temperature as the maximum in the tensile strength, although the results are all from the same specimens. It is of interest that the cold drawing has affected the reduction of area relatively less than the tensile strength and elongation.

Figure 85 shows the effect of temperature on the tensile strength of annealed molybdenum wires of various grain sizes. (The wire described as reduced 96 per cent hot was produced by hot swaging followed by drawing, part of the reduction at least being effected below the recrystallization temperature.) In all wires the tensile strength decreases with rising temperature

throughout the range shown. In the annealed wires, particularly those of medium and coarse grain size, there is a marked horizontal extending from about 100 to 900° C., which is approximately the recrystallization temperature of molybdenum. This may

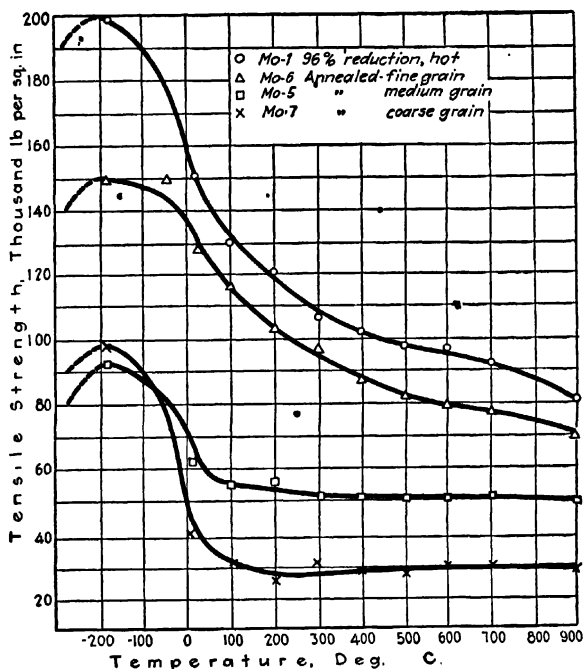


FIG. 85.—Effect of temperature on the tensile strength of molybdenum wires. (Sykes.)

be a manifestation of the blue heat phenomenon. Although tests were not made below the temperature of liquid air, the strength is represented as decreasing at lower temperatures. This fall in tensile strength might be expected to occur at some temperature slightly lower than -185° C., since the tensile strength of tungsten falls between 25 and -185° C. Curves have already been given and discussed showing the effect of temperature on the elongation of molybdenum, in Fig. 68.

Figure 86 shows the effect of temperature on the tensile strength of two kinds of tungsten wire, of which No. 1 has a structure

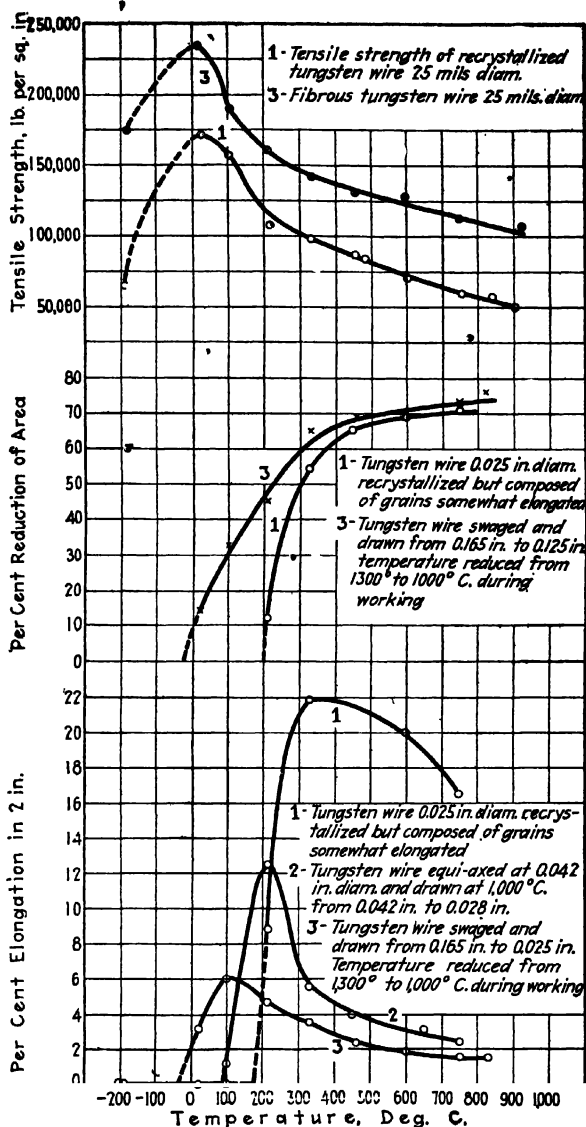


FIG. 86.—Effect of temperature on the tensile strength, elongation, and reduction of area of tungsten wires.

composed of unstrained but slightly elongated grains. Wire No. 2 was produced by swaging and drawing from 0.165 to 0.025 in. at temperatures gradually falling from 1,300 to 1,000° C. The temperatures covered by these curves are entirely below recrystallization. The tensile strength increases on falling temperature, but is lower at -185° C. than at room temperature. Tungsten is the only metal in which this drop has been observed, but, as mentioned above, it probably occurs in most metals at some very low temperature. The actual hardness of the tungsten is probably greater in liquid air than at room temperature and the decrease in strength is probably due to brittleness.

Figure 86 also shows the effect of temperature on the elongation of three kinds of tungsten wire as described in the figure. In all cases the elongation increases on falling temperatures until the region of low temperature brittleness is reached. These curves illustrate particularly well the law that the maximum elongation occurs at lower temperatures the greater the amount of cold working, but that the actual elongation at this maximum decreases as the amount of working increases. Comparing the elongation and tensile strength curves, it will be noted that the development of brittleness is at first accompanied by a sharp rise in tensile strength. This appears to be a rule for all metals.

In both wires shown the reduction of area increases with rising temperature throughout the temperature range given. At all temperatures covered by these tests the reduction of area is greater in the cold-drawn wire than in the annealed wire.

CHAPTER VII

COMPOUNDS OF METALS

The structure of a complex alloy may be analyzed with the microscope and resolved into such elementary parts or constituents as appear to be in themselves physically and chemically homogeneous. Homogeneity is, of course, a relative quality and, since all matter is conceived to be discontinuous, there is no ultimate homogeneity. In alloys, constituents are often encountered which appear under the highest resolving powers of the microscope to be homogeneous, but which are known from other evidence to be physical mixtures.

The constituents finally considered as elementary can be divided into three general classes:

1. Pure metals and metalloids.
2. Compounds.
3. Metallic solid solutions.

The pure ductile metals are important industrial materials and many important alloys, notably the brasses, containing up to about 36 per cent of zinc, consist entirely of a single solid solution. Most alloys, however, are complex in structure, being aggregates of two or more elementary physical constituents. A knowledge of the properties of these constituents is fundamental to an understanding of the properties of the aggregates. It is the purpose of this and the succeeding chapter to discuss the properties and constitution of metallic compounds and solid solutions.

Compounds.—About 80 simple substances are recognized—the chemical elements. All other materials consist of two or more of these elements associated with each other. The various combinations of elements are classed as mixtures, chemical compounds, or solutions, according, in the first place, to their properties, but fundamentally according to the manner in which the elements are associated. The three classes are, in general, quite distinct, but there are regions of overlapping or of uncertainty as to classification.

The manner in which the elements are mixed or associated is the fundamental cause of these distinctions, and should be the ultimate criterion of classification. The atoms of the elements are the physical units of final concern, however, and the manner in which they are associated is not always clear. This classification must, for the present, be based largely on the observed properties of the material.

When two or more substances (elementary or otherwise) are put together in such a way that the specific properties of each ingredient are retained, the product is usually to be regarded as a mixture. Mixtures are often produced by mechanical means and are often separable by mechanical means, but not necessarily so. If a material can be separated into its ingredients by mechanical means, however, it can be definitely classed as a mixture.

If powdered aluminum is stirred into molten sulphur at a temperature just above the melting point of sulphur, no chemical combination or solution takes place, but a suspension of solid particles of aluminum in liquid sulphur is formed. Such a mixture, containing about 15 per cent of aluminum, forms on solidification a material resembling cast aluminum in appearance, and has been used to mend defects in aluminum castings. The useful properties of the mixture depend on the retention of the color and metallic luster of the aluminum, and the fusibility of the sulphur. The mechanical and chemical properties of the material are, of course, chiefly those of the predominant and continuous ingredient, sulphur.

If in the preparation of this material the temperature is allowed to become too high, violent chemical combination takes place with the formation of aluminum sulphide, a substance whose color, fusibility, and other properties differ altogether from those of aluminum and sulphur. If the proportions of aluminum and sulphur taken are just right, the result is a single substance, a chemical compound, instead of a mixture as before.

When substances interact with the permanent loss of some of their specific properties and the appearance of new properties, the product is apt to belong to the class of chemical compounds. The process of chemical combination involves energy changes which are usually of considerably greater magnitude than those involved in physical changes, like fusion and evaporation. The evolution of a large amount of energy is, therefore, indicative of

the formation of a compound. Most important of all, the elements unite to form chemical compounds in definite proportions and only in proportions expressed by their atomic weights, or simple integral multiples thereof.

Solutions.—When a little alcohol is added to water, a solution of alcohol in water is formed, the properties of which are very similar to those of pure water. If the percentage of alcohol is gradually increased, the various properties of the solution, such as density and boiling point, undergo changes which are likewise gradual in nature. It is found that water and alcohol are mutually soluble in all proportions, and that the continuity of the solutions extends from pure water to pure alcohol.

In general, a *solution* may be defined as a mixture or association of substances, homogeneous throughout, the proportions of whose components can be altered gradually without the production of abrupt changes in the properties of the solution. This absence of definite stoichiometrical proportions is one of the chief characteristics which distinguish solutions from compounds.

When two substances form a solution, it is customary to regard that substance which is present in larger amount as the *solvent* and other substance as the *solute*. There is no general fixed rule; there is, for example, no criterion by which to select the solvent in the case of a solution containing equal volumes of water and alcohol. There is a definite rule applicable to most metallic solid solutions, as will be pointed out later.

Gaseous Solutions.—All gases which do not react with each other mix in all proportions to form gaseous mixtures which are to be regarded as solutions. The tendency of gases to diffuse into each other until homogeneity is attained is well known, as illustrated by the upward diffusion of heavy gases, like bromine, against the force of gravity. The even distribution of carbon dioxide in the earth's atmosphere is a result of this diffusion tendency, assisted, of course, by convection currents. From the fact that gases of different densities will diffuse into each other against gravity it follows that a gaseous solution once formed will not segregate on standing, under the influence of gravitational force.

Liquid Solutions.—The tendency to become homogeneous by diffusion is also observed in liquid solutions, although the rate of diffusion is much less than in gases. A closely related phenomenon is the development of osmotic pressure when a solution is

separated from the pure solvent by a semi-permeable membrane or, more generally, whenever a suitable semi-permeable membrane is placed between two different solutions in a common solvent, particularly water. The concentrations of two such solutions can be so adjusted that no osmotic pressure is developed, in which case the solutions are said to be isotonic. The development of osmotic pressure is a manifestation of a tendency of the solution to dilute itself. The causes and mechanism of the phenomenon are not understood, but there is evidently a close relation between osmosis and the process of diffusion in gases and liquids.

It has been found that the osmotic pressure of a substance like sugar in aqueous solution is equal to the pressure which would be exerted by the same quantity of the substance in the form of a gas at the same temperature. In the case of solutes which undergo ionic dissociation in solution, the pressure is greater and is proportional to the number of molecules plus ions in solution. It has always been found that the osmotic pressure is affected by temperature in the same way as gaseous pressure. A corollary of this is that solutions which are isotonic at one temperature are isotonic at all temperatures, as long as there is no change in the constitution of the solution. The fact that the gas laws are directly applicable to substances in solution is probably the greatest generalization that has been made regarding solutions.

The process of solution involves the dispersion of the solute in a way very much akin to its conversion to a gas, and therefore absorbs energy representing the heat of vaporization of the solute, and also the heat of fusion, if the solute is a solid. When a substance dissolves with an evolution of heat, as in the case of sulphuric acid in water, it is to be considered that chemical combination has taken place, in this case the formation of hydrates.

Suspensions and Colloidal Solutions.—If some fine sand and water are shaken together, a suspension is formed which separates quite rapidly on standing, the sand settling to the bottom. The finer the sand the slower does it settle out. A small particle falling through a viscous medium (or rising, if it is lighter than the medium), soon reaches a maximum velocity which thereafter remains constant. Other conditions being equal, this velocity is proportional to the square of the diameter of the particle (Stokes' law). The rate of settling of a suspension therefore

decreases rapidly as the suspended particles become smaller. Suspensions in water of the very fine material which constitutes clay are familiar in the muddy waters of many rivers, and separate on standing only too slowly. Obviously, if the particles of a suspension are sufficiently small, they will remain suspended indefinitely.

Certain suspensions which, like true solutions, remain indefinitely without separating are called "colloidal solutions." The term "colloid" was originally understood to denote a substance which, when pure or mixed with a little water, is gummy and sticky, and which when in "solution" will not diffuse through a parchment membrane. The first requirement, was soon disregarded and, since the inability to diffuse through a parchment membrane appears to be due to the large size of the particles of the solute, the particle size became the final and more logical criterion. A colloid is now defined as a dispersed system of particles, liquid or solid, crystalline or amorphous, whose diameters are from 5 to 100μ ($1\mu = 0.000001$ mm.).

In general, colloidal solutions do not settle out on standing, unless some coagulation first occurs. They exhibit osmotic pressure and diffusion to a very slight extent, if at all. Observations with the microscope and ultramicroscope on suspensions and colloidal solutions in liquids have shown that their particles are in motion in a manner like that of the supposed motion of the molecules of gases. Particles having diameters of about 4μ ($1\mu = 0.001$ mm.) or greater show scarcely perceptible motions. Particles of about 1μ diameter appear to oscillate through distances about equal to their own diameters. When the diameters of the particles are from 10 to 40μ , the distances through which they travel in a straight line are about 20μ . The continuous motion of these particles indicates that the diffusion tendency is present in a colloidal solution.

It is interesting that the metals can be dispersed in liquids to form colloidal solutions. Probably the best known are the colloidal solutions of gold in water, which were first produced by the reduction of gold chloride solutions. A general method for the preparation of colloidal solutions of metals in liquids consists in striking an arc below the surface of the liquid, using electrodes of the desired metal. The colloidal gold solutions exhibit a wide range of colors, from a rich ruby-red to a deep blue. The color is due entirely to the presence of the small particles

of metallic gold, and depends on the sizes of these particles. The red gold solutions gradually turn blue, especially in the presence of an electrolyte. This is due to the growth of the gold particles. It has been shown by the *x*-ray spectrometer that the particles are crystalline in structure.

Colloidal solutions merge into suspensions on one side and into the "true" solutions on the other, without any sharp dividing line except the arbitrary requirement as to particle size (5 to 100 μ) mentioned above. In general, colloidal solutions are thought of as suspensions or emulsions so fine that they will not settle out for a considerable period of time. The individual particles of the colloid are regarded as pieces of sufficient size to possess many of the properties characteristic of the substance, as in the case of the gold solutions, whose particles contain a large enough number of atoms to give the characteristic diffraction pattern of crystalline gold. In the so-called true solutions, on the other hand, it is understood that the solute is dispersed in the form of individual atoms, molecules, or ions.

Condition of Compounds in Solution.—The physical units of a solute in solution are not necessarily the "molecules" represented by the chemical formula. There are few such molecules in solutions of substances which undergo electrolytic dissociation. Nevertheless, in naming the solute in such solutions the name of the substance is used which is precipitated when the solution becomes supersaturated, as by evaporation or temperature change. A solution of ordinary salt in water is spoken of, for example, as a solution of *sodium chloride* even though it is believed that in solution the solute is practically completely dissociated into sodium ions and chlorine ions. It is therefore entirely justified, by usage, to speak of solutions of compounds in metals, even though it may be believed that such compounds are dispersed as atoms of the constituent elements when in solution. The condition of the solute in solution is not always known. What is usually known is the substance which separates from solution when conditions are changed so as to produce supersaturation. It is therefore to be understood that the naming of this substance as the solute does not carry any implication as to its condition in solution.

Chemical Compounds—Strong and Weak.—The various elements possess for each other specific attractions which lead to chemical combination, and which, for want of a more precise

term, are conveniently called "affinities." It is a familiar fact of chemistry that the affinity is greater between dissimilar elements than between similar elements, as shown, for example, by the greater energy of combination and by the formation of more stable compounds.

The metals form definite chemical compounds not only with the dissimilar non-metallic elements but also with the metalloids, and in many cases with each other. The compounds of the metals with each other, called "intermetallic compounds," do not, however, show the marked evidences of chemical combination which are found in the compounds of the metals with the electronegative elements like oxygen and the halogens.

The heats of formation of the intermetallic compounds are, as a rule, very small.

Instability of Intermetallic Compounds.—These compounds generally have an independent existence only in the solid crystalline form. Many of the oxides and halides of the metals can be sublimed, or melted and distilled, without decomposition. If this is attempted with an intermetallic compound, it is usually found that the more volatile element vaporizes first and is gradually lost, very much as though it were merely dissolved in the other element.

The melting of an intermetallic compound is usually sharp, however, and takes place at constant temperature.

Failure of Valence Rules.—While intermetallic compounds contain their constituent elements in definite stoichiometric proportions, these proportions are not necessarily, nor even commonly, in accordance with the ordinary rules of valence. Each metal possesses one or two definite valencies, or capacities for chemical combination, with respect to other elements which are chemically very dissimilar. Thus, copper combines with the monovalent element, chlorine, in two proportions, to form the compounds, CuCl and CuCl_2 , in which the copper has valencies of 1 and 2 respectively. Aluminum forms, readily, only one chloride, AlCl_3 , in which its valency is 3. Yet copper and aluminum combine with each other to form the compound, CuAl_2 , a very important constituent of the light alloys. The valency of copper here appears to be 6, on the basis of a combining capacity of 3 for each atom of aluminum. It is, of course, possible to construct a structural formula which satisfies the ordinary rules of valence, as is done in organic chemistry. This

does not help much, however, especially since there is no basis for assuming a definite molecular weight, a step which is necessary in arriving at a correct structural formula. It has been pointed out before that the conception of molecular weight has little significance in connection with compounds which exist only in the crystalline form. Further discussion of the failure of the application of ordinary valence rules to intermetallic compounds is not necessary. A few formulas will sufficiently illustrate the proposition: Cu_2Zn_3 , Cu_3Sn , Cu_3Al , Mg_2Sn , FeAl_3 .

With the elements of intermediate chemical characteristics, like carbon, silicon, boron, nitrogen, phosphorus, arsenic, and antimony, the metals are more apt to form definite compounds than they are with each other. The compositions of these compounds are sometimes in accordance with the ordinary valencies of the elements, but the correspondence is not sufficiently frequent to be useful in the determination of formulas. The following are some typical compounds of this class: Fe_3C , Mg_2Si , Fe_3P , Cu_3P , and SnSb .

Tammann's Rules.—Tammann has formulated two general rules, based on the periodic system, to indicate what elements will form compounds with each other:

I. Neighboring elements in a natural group (a subgroup of the periodic system) do not form compounds with one another.

II. An element either forms compounds with all the members of a natural group, or with none of them.

The members of the first two short periods are provisionally excluded from these rules, so that each natural group is regarded as consisting of three members. Desch states that the first rule is actually wider in its scope than stated by Tammann, inasmuch as the elements of a natural subgroup, *whether neighboring or not*, do not form compounds with one another, with the single exception of bromine and iodine, (also chlorine and iodine). A good example of the application of these rules is found in the subgroup consisting of copper, silver, and gold.

Rule I. These metals do not form compounds with one another.

Rule II. All of these metals form compounds with Mg, Zn, Cd, Al, Sn, Sb, and Te, but none of them form compounds with Bi, Fe, Co, Ni, or Pd.

Rule II has, however, so many exceptions that its value in prediction is practically nil. The exceptions do not seem to be related in any simple manner to the periodic system. After a

careful consideration of the facts available, Desch concludes that Tammann's first rule is the only generality that has any practical value in the matter of predictions concerning the compounds of metals. Reference should be made to Desch and Tammann for a detailed discussion on the occurrence of intermetallic compounds.

Metallic and Non-metallic Compounds.—Compounds may be divided into two general classes according to whether or not they are appreciably soluble in the molten alloy. Usually, the compounds of the distinctly electronegative elements with the metals are almost insoluble in the liquid metals. This applies to the chlorides, fluorides, oxides, sulphides, silicates, and aluminates, which commonly come in contact with molten metals and alloys. When such compounds are found in solid metals or alloys, they are present as mechanical inclusions, and are referred to as non-metallic impurities. On the other hand, there are some oxides and sulphides which are soluble in the molten metals to an important extent. Among these may be mentioned the oxides of copper, nickel, and silver, and the sulphides of iron and nickel. These would be regarded as non-metallic impurities but not as mechanical inclusions, unless they were present in amounts exceeding their solubilities in the liquid metal at its freezing point.

The compounds of the metals with each other and with the metalloids are more soluble in the liquid metals, and are, consequently, more important as alloy-forming constituents. The properties of these compounds resemble, in general, those of the metals, so the compounds may be described as metallic, as opposed to the non-metallic compounds mentioned above.

Hardness and Brittleness of Compounds.—The most important, and probably the most apparent, characteristics of the compounds of metals found in alloys are their great hardness and brittleness. Alloys made up entirely of such compounds are usually very hard and so brittle that they are useless for mechanical purposes. The rich alloy, or hardener, commonly used for the addition of copper to aluminum contains 50 per cent of copper and therefore consists largely of the compound, CuAl_2 , which contains approximately 54 per cent of copper. This alloy owes its usefulness largely to the fact that it is brittle and can be easily broken up to make the required weights.

The hardness of this compound is indicated by its approximate Brinell hardness of 300, obtained by extrapolation from measure-

ments on alloys of lower copper content. This is to be compared with a Brinell hardness of about 25 for commercially pure aluminum and about 40 for copper.

Brittle Materials Not Necessarily Weak.—Brittle materials are too apt to be considered weak, even when they possess a degree of hardness which is indicative of great inherent strength. It is commonly recognized that hardened tool steel is strong because people are familiar with the results of tests which have shown very high values for tensile strength, in the neighborhood of 300,000 lb. per square inch. Yet, because glass is easily broken, it is commonly considered a weak material, although it is known that its hardness is comparable to that of the hardest steel. In a sense, this common opinion is correct, since it is true that, ordinarily, glass is easily broken, and this means that the piece, as a whole, is at least *effectively* weak. Glass tested in tension in the form of rods a few hundredths of an inch thick shows a strength of 10,000 to 30,000 lb. per square inch. When carefully tested in the form of fibers having a diameter of 0.00012 in., it has shown a tensile strength as high as 492,000 lb. per square inch.

The reason for this discrepancy lies largely in the important effect of eccentrically distributed stress in the testing of brittle materials. A ductile material subjected to eccentric loading quickly adjusts itself by permanent deformation at any points where the stress exceeds the elastic limit, with comparatively little damage. This is not possible in a brittle material and, if the stress at any point in the piece subjected to load exceeds the elastic limit, rupture results. It is obviously easier to avoid such local overstressing in small pieces than in large pieces. This accounts for the fact that many materials which are commonly thought of as very fragile, such as glass, show remarkably high strength when carefully tested in small sections.

Great Inherent Strength of Hard Compounds.—Unfortunately, no direct strength measurements of small pieces of the principal intermetallic compounds, *e.g.*, Fe_3C and CuAl_2 , have been made. It is important to keep in mind that the true strength of such hard, brittle materials, when properly protected against eccentric loading, by their small size and by embedding in a ductile matrix, is very high. It may safely be assumed that cementite (Fe_3C) has a strength of several hundred thousand pounds per square inch. It is chiefly because of the great strength and hardness of

metallic compounds that they are desirable as alloy-forming constituents.

It is also of importance to note that, of all the constituents of alloys, the metallic compounds are the ones whose mechanical properties are least affected by temperature.

Density of Compounds.—The density of a material which is a mechanical mixture or aggregate of two or more constituents can be calculated accurately from the known densities of these constituents, granting, of course, that the aggregate is substantially free from voids. The calculation can be made most conveniently in terms of specific volumes. As an illustration, an alloy of lead and antimony which is made up of practically pure lead and pure antimony may be taken. An alloy containing 15 per cent of antimony by weight will be considered.

Density of lead.....	11.350 g. per cubic centimeter
Specific volume of lead $\left(\frac{1}{D}\right)$	0.088 c.c. per gram
Density of antimony.....	6.700 g. per cubic centimeter
Specific volume of antimony $\left(\frac{1}{D}\right)$	0.149 c.c. per gram
Volume of lead in 100 g. of alloy = 85×0.088 =	7.480 c.c.
Volume of antimony in 100 g. of alloy = 15×0.149 =	2.240 c.c.
Volume of 100 g. of alloy =	9.720 c.c.
Density of alloy = $\frac{100}{9.72}$ =	10.300 g. per cubic centimeter

The expressions "calculated density" and "calculated volume" will be used in referring to values obtained in this manner.

In general, the specific volume of a compound is less than the value calculated from the specific volumes of its constituent elements. This is true to such an extent that, in the case of some "strong" compounds, the volume occupied by a given mass of the solid compound is less than that occupied by the quantity of one of the elements contained in this mass, when existing in the free (solid) state. Such marked contractions are usually not found in weak compounds, like those of the metals with each other and with carbon, phosphorus, etc., but some contraction does seem to be the general rule. Desch gives a contraction of 10 per cent for the compound, Cu_3Sn . The density of cementite (Fe_3C), obtained by calculation from the observed densities of steels, is about 7.59 g. per cubic centimeter. This value is

higher than that calculated from the densities of iron and carbon, even assuming the latter to have the density of diamond. It is certain, too, that the iron and carbon atoms taken together occupy less space in the form of cementite than in the solid solution austenite.

It has been reported that some antimonides and arsenides form with an increase in volume. Apparent expansion may be due to unsoundness (voids), so that these reported expansions must be regarded with some question at present.

Thermal Expansion.—Very little evidence is available on the thermal expansivity of metallic compounds. Reasoning from the general relationship between hardness and coefficient of expansion, the thermal expansion of metallic compounds would be expected to be somewhat less than that calculated from the expansivities of the combining elements.

Melting Point.—It has been mentioned that, as a rule, metallic compounds melt at constant temperature, in which respect they resemble other definite chemical compounds. It is also a general rule that the melting points of these compounds are relatively high, being frequently above the melting points of their constituent elements. An alloy which consists entirely of a definite compound always has a melting point higher than that of other alloys of the series having nearly, but not quite, the same composition.

Electrical Conductivity.—The electrical conductivity of a compound between two metals may be less than that of either metal, or may be between those of the two metals, but it is never greater than that of the best conducting metal. Some compounds seem to have very low conductivity. In general, the temperature coefficient of electrical conductivity of compounds is less than that of pure metals but greater than that of solid solutions.

Magnetism.—Some of the compounds of iron display ferromagnetism, notably the oxide, magnetite (Fe_3O_4), and the carbide, cementite (Fe_3C). This is rather to be expected in view of the marked magnetic properties of iron. It is quite surprising, on the other hand, to find that certain alloys, called the "Heusler alloys," are magnetic although not one of their constituent elements is magnetic. All of these alloys contain manganese, a typical group being made up of manganese, copper, and aluminum. The magnetic properties have been definitely associated with the existence of certain intermetallic compounds.

This is a striking example of the appearance in a compound of properties not found in the constituent elements in the pure state.

Structure of Metallic Compounds.—With the exception of slag inclusions, which may sometimes be vitreous or amorphous in structure, the compounds found in metals and alloys are crystalline. It has been pointed out in a previous chapter that, although it is often easy to retain the amorphous condition of undercooled liquids in oxides, silicates, etc., like silica and the glasses, it is practically impossible to do so in the case of metals.

Particles of intermetallic compounds observed in alloys exhibit many evidences of crystallinity but, because of the restricted conditions under which they form, they usually fail, just as the pure metals do, to show well-defined crystalline forms. It is difficult to obtain pieces of these compounds of sufficient size and perfection of form for goniometric measurements. The investigation of crystalline structure by this means is therefore very limited. Such results as have been obtained show that, in general, the structures of these compounds are very complex as compared with the very simple structures of the pure metals.

The x-ray method of crystal analysis, as developed for powders and fine-grained metals, is applicable to this problem and offers promise of disclosing the internal structures of the intermetallic compounds. Because of the complexity of the structures, however, this method must apparently be supplemented by the Bragg method or other means. Investigations have already been made of the compounds, Fe_3C and CuAl_2 . The following is quoted from a paper by Westgren and Phragmen:¹

Debye photographs of cementite (Fe_3C) and of the well-known crystal tablets of spiegel iron have been found to be identical. A Laue photo and investigations of an orientated rotating crystal of the latter type have made it possible to find out the crystal data of cementite. It belongs to the orthorhombic system, its ratio of axes is 0.670:0.755:1, and the dimensions of its elementary parallelepiped are 4.53, 5.11, and 6.77 A.U. (Angström Units). The base group consists of four molecules of Fe_3C , which corresponds to a specific weight of 7.62 for the cementite.

Hardness and Brittleness Due to Structure.—The complex crystals of the intermetallic compounds do not offer the numerous planes of weakness and easy slip which are present in the pure

¹ "X-ray Studies on the Crystal Structure of Steel," presented at Annual Meeting of the Iron and Steel Institute, May, 1922.

metals. This feature is largely responsible for the hardness (resistance to deformation) and lack of plasticity of the compounds.

Another consideration is important in connection with plasticity. When motion takes place along a slip plane in a pure metal, it is quite easy for the displaced crystal fragments to reestablish cohesion with each other. As long as the motion is one of translation without rotation, the original structure of the unbroken crystal is reproduced every time the fragments move, relatively to each other, a distance equal to the distance between successive rows of atoms. A crystal of a compound is a body whose cohesion depends on a peculiar and complex grouping of its constituent atoms. When such a crystal is ruptured along a cleavage plane, the motion of the fragments through a distance equal to the distance between successive rows of atoms will, in general, produce a configuration of atoms entirely different from that in the original crystal, and one not conducive to the reestablishment of cohesion. The complexity of atomic arrangement in compounds is thus a bar to the maintenance of mechanical continuity during deformation.

It is interesting to note that the first compound formed on the addition of zinc to copper (CuZn) has a simple space lattice, the body-centered cubic, and that this compound possesses considerable ductility.

Atomic Bonds in Compounds.—Knowledge is very deficient in regard to the manner in which atoms are joined to each other, but there is evidence that the nature of the interatomic bonds in metals, compounds, and solid solutions plays an important part in the determination of physical properties, and must eventually be given full consideration. For the present it is possible to do little more than draw analogies and a few interesting, though speculative, conclusions.

It has been pointed out above that compounds are most likely to form between elements which are chemically dissimilar and whose atoms have high specific attractions, or "affinities," for each other. There is evidently a close relation between chemical attraction and the physical attraction which determines mechanical strength. The hardness and strength of a substance are measures of the force required to separate the constituent atoms, and all mechanical strength is based fundamentally on the specific attractions between atoms. It is quite natural to find that compounds made up of atoms which have high specific

attractions for each other exhibit great hardness and strength. High atomic attractions may be overcome by simplicity of atomic arrangement, leading to easy motion along slip planes, but this source of weakness is minimized in compounds by their complex structures.

It is quite probable that some of the electrons are "fixed" when certain intermetallic compounds form, thus giving rise to a condition somewhat similar to that pictured by Hull in connection with a solid salt, like NaCl. Hull considers that the Na atom functions as a positive ion and the chlorine atom as a negative ion, in solid crystalline salt. The cohesion of this substance is due to the attraction of the sodium ions for the chlorine ions. The sodium ions would repel each other, and the chlorine ions would repel each other. The brittleness of such a crystal is due, then, to the fact that slip would bring the chlorine ions opposite one another and the sodium ions opposite one another. Since the like ions repel each other, the crystal cleaves rather than slips.

In metals, the like atoms, which are not here supposed to function as ions, attract each other, and, consequently, new cohesion bonds are established as slip propagates.

In intermetallic compounds slip is hard to start, both because of the high attractive forces between unlike atoms and because of the relatively small number of potential slip planes. The first slip or motion would bring like atoms adjacent to one another. Since these have less mutual attractive force than that required to separate the unlike atoms, that is, to start slip, the fragments could not be held in their new positions and cleavage would result.

Important Compounds of Metals.—The following is a list of some of the more important compounds of metals which are found in the commercially pure metals and alloys, together with a brief account of their occurrence and properties:

Fe₃C.—A carbide of iron, known metallographically as "cementite," possesses great hardness and strength, which render it an important hardening and strengthening constituent in steels and cast iron. It is also quite brittle, and hence imparts brittleness to alloys in which it occupies a commanding position.

Fe₃P.—Iron phosphide. Found in some cast irons but not normally in steels. Hard, strong, and brittle like cementite.

FeS.—Iron sulphide. Appreciably soluble in molten iron and probably somewhat soluble in solid iron. Not normally found in good iron and steel, being converted to MnS by the addition of

manganese. When present confers hot-shortness because of its fusibility and occurrence at the grain boundaries.

MnS.—Manganese sulphide. Normally present in iron and steel. Because of its high melting point and occurrence in the form of isolated globules, it does not impart hot-shortness, as does FeS.

Mn₃C.—Manganese carbide. Similar in properties to Fe₃C and isomorphous with it. Found in steels and cast irons.

FeO.—Ferrous oxide. Occurs in steel which is not thoroughly deoxidized or killed. Is hard and brittle. In moderate amounts probably adds some hardness and strength to the steel.

Cu₂O.—Cuprous oxide. A normal constituent of commercially pure copper. Hard and brittle. Imparts quite an appreciable addition of hardness and strength to copper.

CuZn.—A substance generally classed as a compound, but only moderately harder and less plastic than copper. Forms the basis of the Beta constituent in copper-zinc alloys.

Cu₂Zn₃.—Harder than the above and quite brittle. The basis of the Gamma constituent in copper-zinc alloys. Alloys containing substantial amounts of it are generally too brittle for mechanical uses.

Cu₃Sn.—A hard, strong, and brittle compound found in bronzes. Important as the wear-resisting constituent in bronze bearings.

Cu₃P.—Copper phosphide. A hard, brittle compound present in some of the harder phosphor-bronzes, where it serves as a wear-resisting constituent.

CuAl₂.—A hard, strong, and brittle constituent which bears to the aluminum base alloys a relation analogous to that of cementite in steel.

Mg₂Si.—Magnesium silicide. Another important hardening constituent in the light aluminum alloys. Specifically, hard, strong, and brittle.

SnSb.—A constituent, hard and brittle as compared with tin, occurring in tin-base-bearing alloys, such as babbitt, in which it is an important wear-resisting constituent.

Mg₃Al₂.—Probably the most important hard constituent in the light magnesium base alloys, in which its function is similar to that of CuAl₂ in the Al-Cu alloys.

CHAPTER VIII

METALLIC SOLID SOLUTIONS

If an alloy of pure copper with a small amount of zinc, say 1 per cent is prepared, and its structure is examined under the microscope, it is found that it contains only one constituent, the grains of which appear homogeneous and alike, except for orientation, and quite similar to the crystalline grains of pure copper. Mechanical and physical tests of the alloy show that, in general, its properties do not differ much from those of pure copper. Other alloys can be prepared containing gradually increased percentages of zinc, and it is found that each alloy consists of a single homogeneous constituent whose hardness, strength, ductility, color, and electrical conductivity depart from those of copper in an entirely gradual manner as the percentage of zinc is raised. These homogeneous alloys, whose properties thus vary continuously with composition, are classed as solid solutions of zinc in copper.

Metallic Solid Solutions are Crystalline.—Molten glass is a liquid solution whose properties change continuously as its temperature is lowered, until at room temperature it has acquired the rigidity which is the usual criterion of the solid state. Its constitution is apparently unaltered; it is still a solution. Ordinary glass might, therefore, be called a solid solution, although there are many who consider that such amorphous materials should be classed as undercooled liquids rather than as solids, the term "solid" being reserved for those materials which, because of their crystalline structures, possess *permanent* rigidity. At any rate, the term "solid solution," as used in metallography, is applied only to crystalline materials. Metallic solid solutions, like those of zinc in copper, exhibit all of the evidences of crystallinity which are shown by the pure metals, such as slip bands, etching pits of regular shape, twin crystals, directional reflection of light, and diffraction of x -rays.

Mixed Crystals.—The German "Mischkrystalle" has been applied not only to metallic solid solutions but also to materials

which do not possess the degree of homogeneity which is associated with solid solutions, such as a composite crystal consisting of a core of one substance surrounded by a sheath of another (isomorphous) substance. For this reason, and because the idea of a mere mechanical mixture is conveyed too strongly, the English translation, "mixed crystals," is an objectionable term. Although formerly used to a considerable extent, it is now almost entirely supplanted by the term "solid solution."

Diffusion in Solid Solutions.—One of the most marked characteristics of solutions in general is their tendency to become homogeneous by the process of diffusion. This tendency is abundantly manifested in metallic solid solutions, which are seldom homogeneous as cast, but attain homogeneity by diffusion.

An alloy of copper with 15 per cent of zinc, for example, begins to freeze with the formation of crystalline nuclei of nearly pure copper. As the temperature falls, these crystals grow by the deposition of material gradually richer in zinc. When the alloy is completely solid, it is an aggregate of grains whose zinc content increases gradually from the center to the boundary. On prolonged heating of the casting at a sufficiently high temperature, say 800°C ., diffusion takes place until the alloy is chemically homogeneous throughout. The process of homogenization is greatly assisted by mechanical working, so that it is readily brought about by the ordinary processes of working and annealing incident to the manufacture of brass.

Atom Substitution in Solid Solutions.—When sufficient opportunity is allowed for diffusion, the copper-zinc alloys, or brasses, consist of a single homogeneous constituent until zinc is present up to about 36 per cent. Examined with the x -ray spectrometer, these alloys show only one pattern, that of the face-centered cubic lattice characteristic of pure copper. No signs are found of the presence of crystalline zinc, which is hexagonal, even with over 30 per cent of zinc present. The most simple and natural conclusion is that the zinc atoms are occupying the positions of some of the copper atoms in the face-centered cubic lattice. In other words, zinc atoms have been substituted for some of the copper atoms.

This conclusion is supported by the observed relation between the densities of the alloys and their lattice dimensions. If the lattice kept the same dimensions as that of copper, then the brasses would all have higher densities than copper, since the zinc atom

is slightly heavier than the copper atom. The densities of the brasses are actually less than that of copper, and the cube edge of the copper space lattice is found to increase with the addition of zinc. The density of any given alloy can be readily calculated from the measured lattice dimensions and the atomic weights of zinc and copper, on the assumption that the zinc atoms are replacing copper atoms. Densities so calculated agree with measured densities to a degree which indicates the validity of the assumption.

Chromium is soluble in solid nickel, and alloys containing up to 60 per cent of chromium show only the nickel pattern with the *x*-ray spectrometer. There is no evidence of the body-centered cubic pattern characteristic of free chromium. The chromium atoms must have replaced nickel atoms in the nickel space lattice.

Solvent and Solute.—It is readily apparent that in the case of some metallic solid solutions there is a definite criterion by which to distinguish solvent from solute. The metal whose space lattice persists in the solid solution is to be regarded as the solvent.

This criterion fails when two metals having the same type of space lattice form a continuous series of solid solutions. The solvent may then be arbitrarily defined as that element whose concentration in the solution exceeds 50 atoms per cent.

In general, it seems that the atoms of the solute replace atoms of the solvent, but it is quite possible that in some cases the solute atoms are distributed between the solvent atoms, rather than in place of them. This is especially probable when there is a limited solubility of an element whose atoms are small as compared with those of the solvent, as in solutions of carbon in iron.

Limited Solubility.—When the amount of zinc in the copper-zinc alloys exceeds about 36 per cent by weight, a new constituent appears. The solid solutions containing up to 36 per cent of zinc, which are isomorphous with copper, are designated by the letter "Alpha," and the new constituent which appears on further addition of zinc is called the "Beta" constituent. This constituent also seems to be a solid solution, in that its composition can be varied, within certain limits, without the production of discontinuous changes in properties. The *x*-ray spectrometer shows that the Beta solution has a body-centered cubic lattice, as distinguished from the face-centered cubic lattice of copper

and the hexagonal lattice of zinc. An alloy containing copper and zinc in equal atomic proportions, represented by the formula, CuZn , consists entirely of the Beta constituent. This alloy may be considered to be a definite compound which serves as the basis or solvent for the Beta solid solutions.

The solubility of zinc in copper is thus limited to about 36 per cent, although solid solutions are formed containing higher percentages of zinc, but based on different solvents.

When solid solubility is exceeded, the new constituent which appears is more often a compound than a solid solution. Solid aluminum, for example, will hold in solution a maximum of about 5 per cent of copper. When this amount is exceeded, the compound CuAl_2 appears as an excess constituent. Theoretically, perhaps, no two substances are completely insoluble in each other, and on this basis it might be said that the CuAl_2 holds some aluminum in solution. Practically, however, such solubility is very slight, and the excess constituent may be regarded as a substantially pure compound.

Complete Solubility.—Copper and nickel both crystallize with the face-centered cubic lattice, and with approximately equal lattice dimensions. The solubility of nickel in copper (or copper in nickel) is complete. All of the alloys consist of a single structural constituent, showing a face-centered cubic lattice whose dimensions change gradually from those of pure copper to those of pure nickel.

It is apparent that two metals cannot possess complete mutual solubility in the solid state unless they have the same space lattice. Before the development of the modern conception of solid solutions, it was considered that complete solubility existed between certain pairs of metals which were of different crystalline structure, such as nickel (face-centered cubic) and chromium (body-centered cubic). Sometimes a single apparently homogeneous constituent is seen under the microscope but shown by x -ray analysis to contain two different space lattices. The diagram in Fig. 87 gives the results of spectrographic analysis of the nickel-chromium alloys. Up to more than 60 per cent of chromium, the only pattern observed is that of nickel. From about 65 to 93 per cent of chromium, two patterns—those of nickel and chromium—are observed, showing the simultaneous existence of two different solid solutions. Alloys containing still higher percentages of chromium show only the chromium pattern.

Solubility Limits Vary with Temperature.—The limits of solid solubility in alloys vary with temperature, just as do the limits of solubility of solutes in aqueous solutions.

The solubility of Fe_3C in iron, for example, decreases from about 1.7 per cent at $1,130^\circ \text{C.}$ to 0.90 per cent at 725°C. At

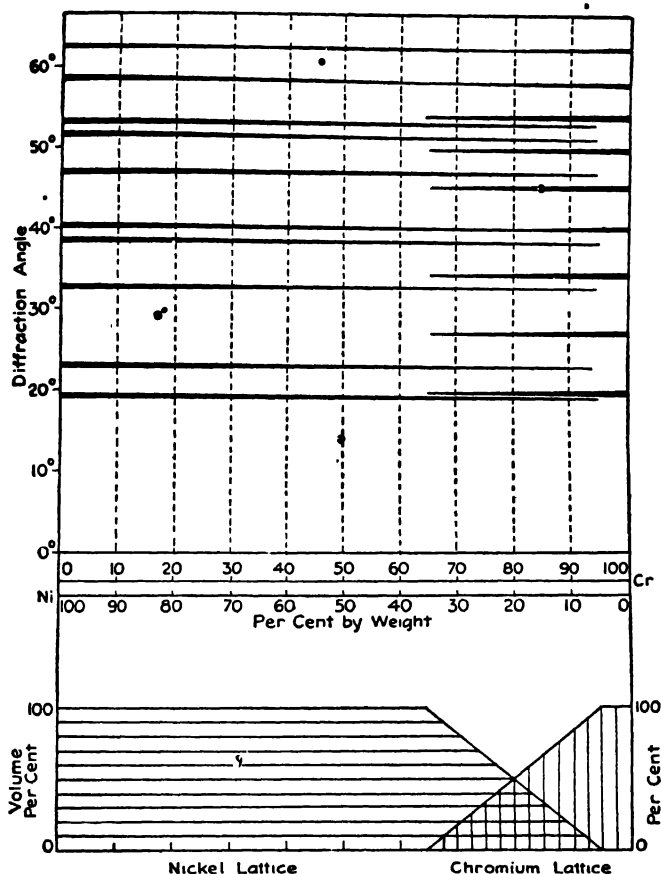


FIG. 87.—Constitution—pattern diagram of nickel-chromium system. (Bain.)

this temperature there is an abrupt change in the constitution of the solid solution, and the solubility falls off abruptly to less than 0.10 per cent.

The solubility of CuAl_2 in aluminum decreases from about 5 per cent at 540°C. to about 2.5 per cent at room temperature.

Solubility does not always decrease with falling temperature. The solubility of zinc in copper (Alpha solution) is about 31 per cent at 900° C. and about 36 per cent at room temperature. A similar direction of change obtains in the Alpha solutions of tin and aluminum in copper.

The direction of the effect of temperature on solubility is governed by the heat effect accompanying solution, in accordance with the generalization of Le Chatelier. If the dissolving of a substance involves an absorption of heat, then a rise in temperature will increase its solubility. If, on the other hand, a substance goes into solution with evolution of heat, then its solubility will decrease with rising temperature.

Ordinarily, the process of solution is an energy-absorbing process. As has been pointed out above, the dispersion of a solute in solution is analogous to its vaporization, and hence requires energy. There are some substances, however, which dissolve in water with an evolution of heat. This is generally considered to be due to the formation of hydrates.

Conditions in metallic solutions differ quite materially from those in aqueous solutions. The formation of complex molecules, or even the existence of such molecules, in solution is usually not to be considered. On the other hand, it is possible that in some cases the dissolving of a constituent does not really involve increased dispersion. The saturated (Alpha) solution of zinc in copper, for example, contains approximately 1 atom of zinc to 2 atoms of copper. The phase or constituent with which this solution is in equilibrium is the Beta constituent. The Beta constituent is a solid solution based on the compound CuZn as a solvent, in which copper can be regarded as the solute. The dispersion of the copper in the pure solvent is indicated by the atomic ratio, *i.e.*, 1 atom of copper to 1 atom of zinc. Consider a Beta solution of the composition assumed for the Alpha solution, that is, one containing a total of 2 atoms of copper to 1 of zinc. One of these 2 copper atoms might be regarded as a solute atom and the other as a solvent atom. The concentration of the *solute* would then be expressed as 1 atom of solute to 2 atoms of solvent, exactly as in the case of the Alpha solution of 1 atom of zinc to 2 of copper. The Alpha and Beta solutions assumed may, therefore, be regarded as of comparable dilution. The heat effect of a change from one to the other would be difficult to predict, on the basis of the relative degrees of dispersion of the solute.

When the excess constituent is a substantially pure compound, as in the case of Fe_3C and CuAl_2 , this consideration is not involved. The passing of carbon from crystalline Fe_3C into solution in iron obviously represents increased dispersion of the carbon atoms, and the disappearance of crystalline CuAl_2 , the copper going into solution in the aluminum, evidently results in increased dispersion of the copper atoms.

The facts seem to be in accord with these considerations. Those cases in which the concentration of the solute in the saturated solid solution decreases with rise in temperature are generally cases in which the excess constituent in equilibrium with the solution in question is itself a solution. When the excess constituent is a substantially pure compound, metal, or metalloid, its solubility, as a rule, increases with rising temperature.

The magnitude of the effect of temperature on solid solubility is more difficult to predict than the direction of the effect.

Solidification and Melting of Solid Solutions.—Solid solution alloys generally freeze and melt throughout a range of temperature, in contradistinction to pure metals, chemical compounds, and eutectic mixtures, all of which freeze and melt at constant temperature.

The freezing point of a metal may be either lowered or raised by the addition of an element which goes into solid solution in it. Thus, the freezing point of copper is raised by the addition of nickel but lowered by the addition of manganese. Both nickel and manganese have melting points higher than that of copper.

When a molten alloy capable of forming a solid solution cools to a certain temperature, solidification begins with the formation of crystals which do not have the composition of the liquid alloy, but are richer in the element whose addition to the alloy would raise its freezing point. In the cases just mentioned, the first solid to form from a molten alloy of copper and nickel would be richer in nickel than the alloy as a whole; while the first solid to form from a molten alloy of copper and manganese (provided the alloy contained less than a certain critical amount of manganese, which produces a minimum freezing point) would be richer in copper than the alloy as a whole.

The separation from the melt of solid material of a different composition from the average composition of the alloy results in an enrichment of the melt in that constituent whose addition to the original alloy would have lowered its freezing point.

From the melt thus enriched, further solidification takes place only after a fall in temperature. The solidification of the alloy continues in this manner while the temperature gradually falls.

The solidified alloy is not of uniform composition, because of this progressive manner of freezing, unless the rate of cooling is so slow that homogenization by diffusion keeps pace with solidification. This is ordinarily not the case, but the "cored" alloy can be rendered homogeneous by annealing, as described in the discussion of diffusion. On reheating such a homogenized solid solution, melting takes place by a gradual process which is essentially a reversal of the freezing process. Melting begins at spots within the grains and at the grain boundaries, the first liquid to form being richer than the alloy as a whole in that element, the addition of which to the molten alloy would lower its freezing point. The crystals continue to melt gradually throughout a range of rising temperatures, which under conditions of equilibrium are identical with the temperature range of solidification.

Reference was made above to the fact that a certain alloy of copper and manganese has the lowest freezing point of the series. Similar minima are found in other solid solution systems, an alloy containing 80 per cent gold and 20 per cent copper, for example, having the lowest freezing point in the copper-gold series. These solid solution alloys of minimum freezing point solidify and melt at *constant temperature* and without the segregation due to progressive solidification.

Annealing Temperatures of Solid Solutions.—The recrystallization temperature of a metal is generally raised by the addition of a solute. The recrystallization temperature of copper, for example, is raised by the addition of zinc, in spite of the fact that both the recrystallization temperature and the melting point of zinc are lower than those of copper.

If, however, the solute has a markedly lower recrystallization temperature than the solvent, and dissolves in sufficiently large quantities, then its low recrystallization temperature may finally assert itself and the solid solution may recrystallize at lower temperatures than the solvent. Copper and nickel are completely soluble in each other in the solid state. The recrystallization temperature of copper is about 200° C., while that of nickel is about 600° C. The addition of a few per cent of nickel to copper raises the recrystallization temperature of the copper

gradually, but considerable nickel must be added before the recrystallization temperature of the alloy is as high as that of pure nickel. If nickel be regarded as the solvent in these solutions, and copper as the solute, then it may be said that the addition of copper to nickel, in sufficient quantities, lowers its recrystallization temperature. In general, the recrystallization temperature of a solid solution is higher than that of its lowest melting constituent, but not necessarily as high as that of the constituent of higher melting point.

When the melting point of a metal is lowered by the addition of a solute, the temperature at which it can be annealed is thereby

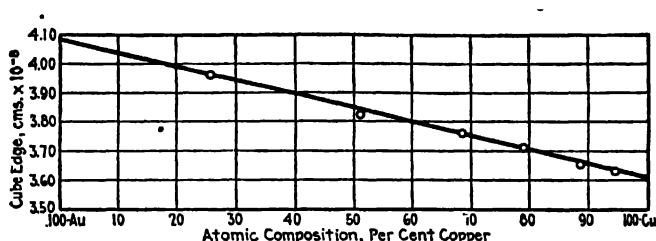


FIG. 88.—Size of fundamental cube in the copper-gold series. (Bain.)

restricted, and since its recrystallization temperature is at the same time raised, the result is a narrowing of the temperature range for annealing. There is not as much latitude in the annealing of the Alpha solid solutions of zinc, tin, and aluminum in copper as there is in the annealing of pure copper.

Density of Solid Solutions.—It appears that the densities of binary solid solution alloys are usually equal to or greater than the values calculated from the densities of the constituent elements. In alloy systems in which the constituent elements are completely soluble in the solid state, there seems to be a tendency for the actual densities of the alloys to correspond closely with the calculated densities. This is true, for example, in the following systems: gold-silver; copper-nickel; tungsten-molybdenum; and gold-copper. The effect of composition on the length of the elementary cube edge is shown graphically for the copper-gold alloys in Fig. 88.

The solid solutions of zinc, tin, and aluminum in copper have densities higher than the calculated values. Table XII shows observed and calculated values for the copper-zinc alloys:

TABLE XII.—DENSITIES OF COPPER-ZINC ALLOYS

Per cent zinc	Density, by American Brass Co.	Density, by Bureau of Standards	Calculated density (by rule for mixtures)
0.00	8.930		
3.00	8.892	8.890	8.87
5.00	8.867	8.866	8.82
10.00	8.807	8.804	8.72
15.00	8.745	8.734	8.62
20.00	8.679	8.667	8.52
25.00	8.599	8.594	8.42
28.00	8.568	8.553	8.37
30.00	8.533	8.528	8.33
32.00	8.502	8.29
33.33	8.493	8.476	8.26
35.00	8.478	8.460	8.23
37.00	8.437	8.437	8.20
40.00	8.396	8.14

The space lattices of some of these brasses have been determined by the *x*-ray spectrometer, and, as mentioned above, the densities calculated from the lattice dimensions agree very well with the observed values.

Since the Alpha brasses are less dense than copper, in spite of the greater atomic weight of zinc, the lattice dimensions are larger than those of copper. This expansion of the copper space lattice by the insertion of zinc atoms seems quite natural in view of the larger atomic volume of zinc. Similar expansions are noted in the Alpha solutions of tin and aluminum in copper. As in the case of the copper-zinc alloys, however, the increase in lattice size is not as great as that calculated from the atomic volumes of the elements. Five atoms per cent tin should increase the volume of the copper 9.3 per cent, but actually the increase is only 4.6 per cent. The addition of 18.8 atoms per cent of aluminum should cause a volume increase of 7.5 per cent, but the actual increase is only 2.8 per cent. It is notable that in all of these cases intermetallic compounds form when the solubility is exceeded.

Whether or not such contractions are general in alloys showing limited solubility and forming intermetallic compounds when the solid solubility is exceeded is not known. It might appear

that the volume contractions just described are due to a resistance of the copper to a change in lattice dimensions, since the atoms of zinc, tin, and aluminum are all larger than the copper atom, and the stretching of the copper lattice is in all cases less than the amounts calculated from the atomic volumes. If this were the case, however, it would be expected that the addition of a smaller atom to a solvent would decrease its lattice dimensions less than the calculated amount. Measurements have been made by Bain on silver-zinc alloys which indicate that this is not true. Zinc dissolves in silver in the solid state, a compound being formed when the limit of solid solubility is exceeded. The atomic volume of zinc is less than that of silver. There should, therefore, be a contraction of the silver lattice on the addition of zinc. The actual contractions observed are greater than those calculated from the rule for mixtures.

It thus seems from the limited evidence available that the general tendency is for solid solutions of metals which are completely soluble in each other to have densities about equal to those calculated from the densities of the metals; when solid solubility is limited and the excess constituent is a compound, the solid solutions tend to be more dense than calculated.

Thermal Expansion of Solid Solutions.—The thermal expansions of solid solution alloys do not differ greatly from the values calculated from the volume percentages of the constituent metals. The tendency is, however, for the expansion to be less than the calculated amount. For example, the Smithsonian Physical Tables give the coefficient of linear expansion of copper at 40° C. as 0.1678×10^{-4} per degree Centigrade; of zinc at 40° C. as 0.2918×10^{-4} per degree Centigrade; and of a 72 Cu-28 Zn brass at 40° C. as 0.1859×10^{-4} . The calculated value for this brass on the basis of the expansivities of pure copper and zinc would be about 0.209×10^{-4} . As compared to changes in electric resistivity and hardness, the usual changes in thermal expansivity are relatively slight and are to be considered somewhat on a par with density changes.

A remarkable and seemingly abnormal change in thermal expansivity is found in the solid solution alloys of iron and nickel. Iron alloys containing more than about 25 per cent nickel retain the Gamma (face-centered cubic) lattice at ordinary temperatures, even if cooled slowly from a high temperature. With about 36 per cent nickel and 0.15 per cent carbon the alloy

(called *invar*) retains approximately constant volume throughout the temperature range represented by extremes in weather conditions. The coefficient of thermal expansion of iron is 0.0000121 and that of nickel 0.0000128 per degree Centigrade at 40° C. The coefficient of thermal expansion of invar varies from plus 0.0000025 to minus 0.0000005 per degree Centigrade. Invar is of great utility where low coefficient of expansion is desirable. Heating several hundred degrees and cooling to room temperature does not always restore the original length of invar parts. The alloy is preferably used where only moderate changes in temperature are encountered. With a nickel content below or above 36 per cent, the coefficient of thermal expansion is higher than that of invar. A solid solution alloy containing about 46 per cent nickel and 54 per cent iron serves as the core of a "dumet" wire used for "leading in" wires of electric incandescent lamps. Platinum was formerly used for this purpose because its coefficient of thermal expansion is nearly the same as that of glass. The above alloy coated with a small amount of copper has the proper expansion and is much cheaper than platinum.

No adequate explanation of the low coefficient of thermal expansion of these iron-nickel alloys has been offered. It is the general consensus of opinion, however, that it is in some way connected with the suppression of the transformation of the face-centered cubic variety to the body-centered cubic variety of iron.

Electrical Conductivity of Solid Solutions.—Alloys of the solid solution type are of great industrial importance because of the high electrical resistivity attainable. The curve in Fig. 89 shows the relation between electrical conductivity and composition for the copper-gold alloys. The conductivity of each metal is lowered rapidly by the addition of the other, the lowest conductivity of the series being reached when the two elements are present in approximately equal atomic concentrations. This curve is typical of binary systems the component elements of which form continuous series of solid solutions.

The increase in the resistivity of a metal by the addition of a solute appears, in general, to be greater the higher the specific resistivity of the solute. Consider, for example, the copper-nickel alloys. The highest resistivity of the series occurs in an alloy containing approximately 50 atoms per cent of each ele-

ment. The resistivity of this alloy is about 30 times that of copper, but only about 5 times that of nickel. The addition of nickel to copper has thus increased the resistivity of copper at a much more rapid rate (per atom of solute) than the addition of copper has increased the resistivity of nickel.

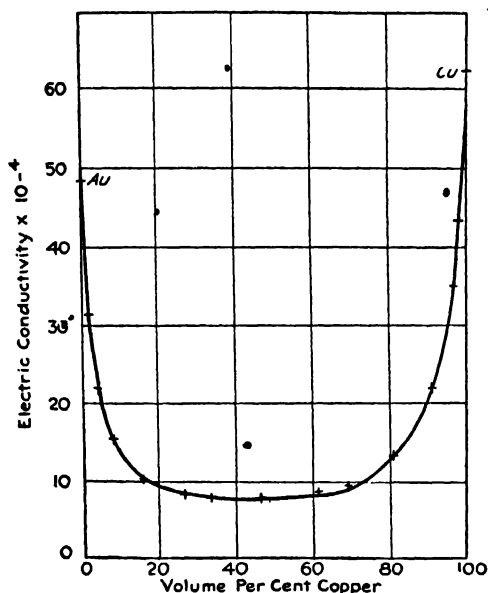


FIG. 89.—Electrical conductivity of copper-gold alloys.

The electrical resistivity of a binary solid solution is usually further increased by the addition of a third element which enters into the solid solution.

Coefficient of Resistance.—The temperature coefficient of electrical resistance is very much less for solid solutions than for pure metals, reaching a minimum, in a given series of alloys, at a composition near that having the highest specific resistance. The curve relating coefficient of resistance to composition is thus roughly parallel to the curve for conductivity, but the effect of the solute on the coefficient is generally even more marked than upon the conductivity. The alloy containing 55 per cent copper and 45 per cent nickel has a conductivity equal to about one-thirtieth ($\frac{1}{30}$) that of copper, and a coefficient of resistance about one seven-hundredth ($\frac{1}{700}$) that of copper.

Some solid solution alloys actually have negative coefficients over certain ranges of temperature.

Commercial Resistance Alloys.—All of the electrical resistance wires on the market, whether for the dissipation of electrical energy or for heating elements, are made of solid solution alloys or of alloys consisting largely of solid solutions. High specific resistivity and low coefficient of resistance are desirable for both of these purposes. Some of the wires possess such low coefficients that standard resistance coils made of them can be used under ordinary variations of temperature without any correction.

Table XIII gives values for composition, resistivity, and temperature coefficient for a number of commercial resistance alloys, including those used for standard resistances, for electrical energy dissipation, and for heating elements.

TABLE XIII.—PROPERTIES OF RESISTANCE ALLOYS

Material	Composition	Resistivity, microhms cm ²	Temperature coefficient		
			0-100° C	At 100° C	At 500° C.
Copper.....	1 72	0.0040		
Constantan, Copel Advance, Ideal . . .	Cu 55% Ni 45%	50 00	0 000006		
Manganin	Cu 84, Ni 4, Mn 12	44.00	-0 000042		
Therlo	Cu 85, Mn 13, Al 2	46 70	0 0000104		
Climax.....	Fe 72, Ni 28	87 00	0.0007		
Chromel A..... Nichrome IV.	Ni 80 Cr 20	104 00	. . .	0 00020	0.00020
Chromel B Nichrome III . . .	Ni 85 Cr 15	89 00	. . .	0 00018	0.00022
Chromel C . Nichrome .	Ni 61, Fe 25 Cr 11, Mn 3	109 00	. . .	0 00023	0.00022

The highest resistivity given is 109 microhms per cubic centimeter for Chromel C. This is obtained by the addition of three solutes to a solvent (nickel) possessing initially a relatively high resistivity.

Mechanism of Metallic Conduction.—Metallic conduction of electricity is supposed to take place by the actual passage of free

electrons through the conducting metal. According to Bridgman,¹ no resistance is encountered by the electrons on passing through the atoms of the conductor, all of the resistance being due to the effort required for the passage of the electrons from atom to atom.

The decrease in the resistance of a pure metal with fall in temperature is then considered to be due to improved contact between the atoms. Lead becomes a "permanent conductor" at the temperature of liquid helium; that is, its resistance is practically zero. The interpretation of this phenomenon is that the lead atoms continuously touch each other at this temperature, and hence offer little or no resistance to the passage of electrons from atom to atom.

Theory of Resistivity of Solid Solutions.—The following is quoted from Bridgman:

The other class of alloys is one in which mixed crystals (solid solutions) are formed, the atoms of the two metals entering side by side into the same crystal edifice. This is possible because of a certain degree of resemblance of the two kinds of atoms. The resemblance is not complete, however, and the indiscriminate use of either kind of atom in the crystal edifice is possible only with a certain amount of distortion in the final result. It is a fact that most mixed crystals will not accept an unlimited amount of the foreign ingredient, but the two atoms will crystallize side by side only up to certain limiting proportions. In the mixed crystal structure we would expect, therefore, a certain amount of imperfect fitting between adjacent atoms, with the result that the electrons encounter difficulty in passing from atom to atom, so that, because of the extra resistance of the "gaps" between the atoms, the resistance of the alloy is greater than that computed from the components (by the rule of mixtures). This is in exact accord with the experimental facts.

Bridgman further points out that the low temperature coefficient is a natural consequence of imperfect fit because temperature changes would not be expected to affect the degree of fit greatly. "This merely means that the gaps between the different kinds of atoms persist to low temperature, as we would certainly expect."

Hardness vs. Resistivity.—It is a fairly general rule that a change in the condition of a metal or alloy which involves an increase in mechanical hardness also involves an increase in

¹ BRIDGMAN, P. W., "The Electrical Resistance of Metals," *Phys. Rev.*, vol. 17, pp. 177-179, 1921.

electrical resistivity. Cold working increases the resistivity as well as the hardness of pure metals and of alloys. The hardening of ordinary carbon steel by quenching is accompanied by an increase in electrical resistivity. When the hardened steel is reheated to certain higher temperatures, both hardness and resistivity diminish. The addition to a metal of an element which enters into solid solution increases its hardness and its electrical resistivity. Bridgman writes:

It has been observed that, as the proportions of the components change through a series of alloys forming mixed crystals, the electrical resistance increases in that direction in which the mechanical hardness also increases. Now an increased mechanical hardness means an increased staggering in the positions of the atoms in the crystalline grains, so that it is more difficult to produce sliding of one part of the crystal on another, and by the same token an increase in the difficulty of the electrons in making the leap from atom to atom.

Bridgman also calls attention to the conditions of atoms on slip planes in cold-worked metals, causing an increased resistance to the passage of electrons from one atom to another.

In connection with the hardness and electrical resistance of cold-worked metals and of solid solution alloys, it should be pointed out that the hardness of a pure metal can be doubled by cold working without increasing the electrical resistance more than a few per cent, whereas a solid solution having twice the hardness of the solvent metal has an electrical resistivity several hundred per cent higher. This is striking evidence of the general proposition that metallic conduction depends on the conditions immediately surrounding the atoms, while hardness depends largely on the relative dispositions (different orientations or registry of slip planes) of relatively large groups of atoms.

Free Electrons in Solid Solutions.—It is assumed by Bridgman in his interpretation of the electrical resistance of solid solution alloys that the number of free electrons is equal to the number calculated by simple proportion from the number of free electrons in the pure constituent metals and, furthermore, that the number of free electrons does not change to any marked extent with temperature. The present authors would point out that the formation of a solid solution may well involve the “fixing” of some of the free electrons of the component metals.

Graphite is a fair conductor of electricity and must be considered to have free electrons, whereas diamond, which is built of the same kind of atoms as graphite, is a non-conductor. The inference is that in diamond there are few free electrons. The carbon atoms are, on the average, much more closely packed in diamond than in graphite. Here is a case where an allotropic change in an element apparently causes a tremendous change in the number of free electrons. It is probable that the great hardness of diamond is due, in part, to cohesion bonds which utilize and thus fix the free electrons.

If such differences in electrical conductivity, and supposedly in the number of free electrons of an element, can accompany an allotropic change, it is not unreasonable to consider that the formation of a solid solution may change the number of free electrons.

It would be expected that there would be fewer free electrons in the solid solution than the number calculated from the constituent metals. The fixing of electrons would be regarded as due to the formation of bonds between the solvent and solute atoms somewhat analogous to the interatomic bonds involved in chemical combination. These bonds would be regarded as contributing to the hardness of solid solutions. Increase in temperature might increase the number of free electrons because of partial dissociation. Both the low conductivity and the low temperature coefficient of solid solutions could be partly accounted for in this way.

Conductivity of Copper.—Because of the predominating use of copper as a commercial electrical conductor, considerable interest attaches to the effect of various impurities on its conductivity. Since many of the common impurities occur in solid solution in the copper, this question is also of theoretical interest in the attempt to trace general relationships.

In considering any data on the effect of a solute on electrical conductivity, it must be remembered that the effect is not a linear one, but becomes less as the amount of solute increases. That is, the effect of a given amount of a solute is greater the less the total amount of the solute present. It seems most logical to compare the effects of various solutes on the basis of equal atomic concentrations.

Data from various sources on the conductivity of copper, as affected by impurities, are not in complete agreement. Some

of the discrepancies are perhaps due to variations in the content of oxygen or other impurities besides the one under special consideration. The agreement is quite good, however, with the exception of one or two elements, in regard to the order in which the various elements should be placed as affecting the conductivity of copper.

Table XIV shows the effect, of 2 per cent by weight, of various metals on the electrical conductivity of copper. The values were taken from the "Physical Chemistry of the Metals," by Schenck and Dean (page 76). Since the conductivity value given for copper is for 0°C ., it seems likely that the other values refer to the same temperature. The authors have assumed the correctness of the values given by Schenck and Dean and have calculated the atomic per cents, volume per cents, electrical resistivities, and the approximate percentage increase in resistivity of copper by the addition of 1 atom per cent and 1 volume per cent of each element. This calculation was made on the assumption that the change in resistivity of copper is a linear function of the amount of added metal, an assumption which, as mentioned above, is not rigidly correct. The values given, however, should be of the right order of magnitude.

From the last two columns of Table XIV it will be seen that the various solutes differ markedly with respect to the rate at which they increase the resistivity of copper. They are arranged in the order of increasing effect, per atom, in Table XV. In the second column of this table, headed *RV*, the elements are numbered in the order of increasing effect on the resistivity of copper, for 1 per cent by volume of the solute. The order is the same as for atomic per cent, with the exception of tin and nickel. From other information available to the authors, it seems probable that up to 1 atom per cent iron increases the resistivity of copper more rapidly than does manganese.

In the remaining columns of Table XV, the solutes are numbered according to the order of various other properties, for purposes of comparison.

According to Bridgman's hypothesis that electrical resistance is due to the effort required for the electrons to jump from atom to atom, it might be supposed that the addition of a solute which distends the copper lattice would increase the resistivity more than the addition of a solute which causes a contraction of the copper space lattice. The effect of a solute on the lattice dimen-

sions of a solvent is indicated by the atomic volume of the solute. In the column headed *AV*, the solutes are numbered in order of increasing atomic volume. It will be noted that this order bears no apparent relation to the order of increasing effect on resistivity. Nickel and iron, which have comparatively large effects on resistivity, have atomic volumes smaller than that of copper, and cause a contraction of the copper space lattice. All of the other elements in the table have atomic volumes larger than that of copper.

The column headed *AW* discloses no relation between atomic weight and effect on resistivity.

In column *H* the solutes are numbered according to increasing effect on hardness. Iron and gold are omitted from this classification because of lack of definite information. The effects of the solutes on resistivity do not, in general, parallel their hardening effects. If only those elements which form compounds with copper are considered, i.e., zinc, aluminum, and tin, the hardening effects do parallel the resistivity effects.

On the hypothesis that resistivity increases (Bridgman) and solubility limits (Rosenhain) are determined by the lattice distortion or disarrangement brought about by the presence of the solute atoms, it might be expected that the effect per atom of a given solute on the resistivity of the solvent would be greater the less the solubility of that solvent. In the column headed *Sol.* the elements are numbered according to their order of decreasing solid solubility, as expressed in atoms per cent. It will be noted that this order does not correspond to the order of increasing effect on electrical resistivity, unless the consideration is again restricted to zinc, aluminum, and tin.

The nearest approach to a general relationship seems to be between the specific electrical resistivity of the solute itself, and its effect on the resistivity of copper, as seen by comparing columns *R* and *SR*.

The correspondence is again not complete. The most conspicuous exceptions are zinc and manganese. If only those elements which have the same space lattice as copper are considered, namely, the face-centered cubic, the rule holds good that the effect of the solute on the resistivity of the solvent increases with the specific resistivity of the solute.

TABLE XIV.—RESISTIVITY OF COPPER-RICH SOLID SOLUTIONS AT 0° C.
(Each alloy listed contains 2 per cent by weight of the solute mentioned)

Solute	Atomic per cent of solute	Volume per cent of solute	Electrical conductivity $\times 10^{-4}$	Electrical resistivity $\times 10^{-6}$	Approx. increase in resistivity per atom per cent of solute, per cent	Approx. increase in resistivity for 1 per cent of solute by volume, per cent
Pure copper.....	62.1	1.61		
Ag.....	1.20	1.700	55.1	1.81	10.0	7.5
Au.....	0.65	0.935	47.5	2.10	46.5	32.0
Zn.....	1.98	2.500	45.0	2.22	19.5	15.0
Sn.....	1.08	2.450	26.5	3.77	124.0	55.0
Ni.....	2.15	2.000	26.0	3.84	64.0	70.0
Al.....	4.55	6.300	17.0	5.88	58.0	42.0
Mn.....	2.30	2.400	12.0	8.34	180.0	174.0
Fe.....	2.25	2.300	13.0	7.70	167.0	165.0

TABLE XV.—COMPARATIVE DATA ON SOLUTES IN COPPER

Solute	R	RV	AV	AW	Sol.	H	SR	Crystal structure
Silver.....	1	1	6	6	7	5	1	Face-centered cubic
Zinc.....	2	2	4	5	4	1	5	Hexagonal
Gold.....	3	3	7	8	2	..	2	Face-centered cubic
Aluminum....	4	4	5	1	5	3	3	Face-centered cubic
Nickel.....	5	6	1	4	1	2	6	Face-centered cubic
Tin.....	6	5	8	7	6	6	8	Body-centered tetragonal
Iron ..	7	7	2	3	8	..	7	Body-centered cubic
Manganese ..	8	8	3	2	3	4	4	Not known

R—Order of increasing effect on electrical resistivity per atom of solute.

RV—Order of increasing effect on electrical resistivity for 1 per cent. by volume of solute.

AV—Order of increasing atomic volume.

SR—Order of increasing specific resistivity.

AW—Order of increasing atomic weight.

Sol.—Order of decreasing solid solubility, in atoms per cent.

H—Order of increasing hardening effect, iron and gold omitted.

Hardness and Strength of Solid Solutions.—The hardness and strength of metals are increased by the presence of solutes in solid solution. This effect is to be observed in many common alloys, the most familiar illustration perhaps being found in the properties of the Alpha brasses. No single set of values can be given as describing completely the mechanical properties of a

pure metal or a solid solution alloy, since these properties vary with grain size and are affected by the form and size of test specimen. The hardening effect of zinc on copper may, however, be indicated by the following values for metal in the worked and annealed condition, with what might be called "normal" grain size:

	TENSILE STRENGTH, POUNDS PER SQUARE INCH	BRINELL HARDNESS
Pure copper	30,000	35
70-30 brass	45,000	55

When two metals form a continuous series of solid solutions, the hardness of each is increased by the addition of the other, the alloy of maximum hardness usually containing about 50 atoms per cent of each metal. The hardness-composition curve of the gold-silver alloys, shown in Fig. 90, is typical.

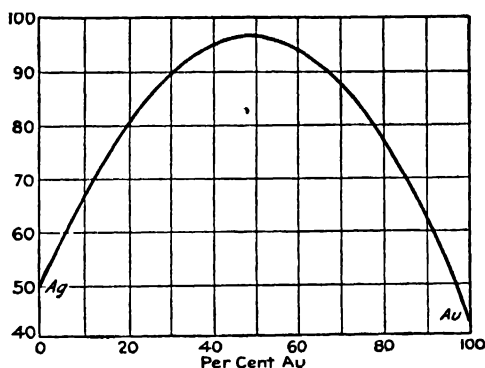


FIG. 90.—Hardness of silver-gold alloys.

In cases of limited solubility, the tendency is for the hardness to increase with the concentration of the solute in solution. Information is lacking in regard to solid solution alloys containing high concentrations of a solute of limited solubility, because in the most familiar alloys of this type the extent of the solubility is relatively low. Among the common alloys the widest range of composition is probably found in the Alpha brasses, where the solubility limit for zinc is about 37 per cent by weight, which is equivalent to 36.3 atoms per cent. The tensile strength of these Alpha solid solutions increases with the zinc content up to the limit of solubility. It has been reported that there is a slight

maximum in Brinell hardness at about 20 per cent zinc. This may be due to an effect of zinc on the grain size. Considering the entire group of properties which are connoted by the general term "hardness," it seems that the hardness of the copper-zinc Alpha solid solutions, in this sense, increases continuously with their zinc content.

Specific Hardening Effects.—The hardening effects of various solutes on a given solvent are quite different, and bear no apparent relation to the hardnesses of the solutes themselves. This is true whether the effects of equal weight percentages, equal volume percentages, or equal atomic percentages of the solute are considered.

It has been postulated by Rosenhain that the hardening effect of a solute on a given solvent metal is closely and inversely related to its limiting solid solubility. That is, the greater the maximum solubility of the solute, the less is its hardening effect per atom added. Rosenhain illustrates the principle in the following:

An examination of the well-studied alloy systems in which the limits of solid solubility have been reliably determined will show that this generalization holds good. If the copper alloys are taken, the hardening effect, within the range of solid solubility in each case, of alloying metals may be placed in the following order: nickel, manganese, zinc, aluminum, tin. The limits of solid solubility, in atomic per cent, for these metals are nickel, 100; manganese, 100; zinc, 36; aluminum, 14; tin, 6.7. In the case of nickel and manganese, although there is an unbroken series of solid solutions in both cases, the shape of the liquidus curve of the copper-manganese system indicates that the formation of a eutectic near the middle of the series is only just avoided; an alteration of pressure, for instance, might easily result in the formation of two separate phases—probably a eutectic. The solid solubility of nickel in copper may, therefore, be fairly regarded as being greater than that of manganese. A similar rule holds for the alloys of aluminum; zinc forms a much longer range of solid solutions with aluminum (up to 15 atomic per cent) than does copper (up to 1.5 atomic per cent), and their hardening effect is in the inverse order. In the alloys of iron, in so far as they have been studied apart from the effect of carbon, a similar law holds good.

There is perhaps some question as to the order of arrangement of the solutes with respect to their hardening effects. Norbury has recently determined the effects of various elements in solid solution on the hardness of copper, and up to 3 atoms per

cent of each element the following order of increasing hardening effect is reported:¹

TABLE XVI.—HARDENING EFFECTS OF SOLUTES IN COPPER

Solute	Maximum solubility in atoms per cent	Hardening effect	
		From Rosenhain's rule	Reported by Norbury
Nickel.	100.0	1 •	2
Manganese	100.0	2	5
Zinc.	36.0	3	1
Aluminum.	14.0	4	3
Silicon.	9.0	5	4
Tin.	6.7	6	7
Silver.	3.0	7	6

The correspondence is here found to be approximate, but not exact. If those elements which do not form compounds with copper (Ni, Mn, and Ag) are omitted, it will be noted that the remainder of the list conforms to Rosenhain's rule.

It seems that the temperature of test should be considered in connection with this question. The specific hardening effects of zinc and nickel, for example, appear to be quite similar at room temperature, but it is obvious that nickel is a far more effective hardener at high temperatures. Perhaps at very low temperatures the hardening effect of zinc is considerably greater than that of nickel.

Plasticity of Solid Solutions.—The plasticity of a metal is, in general, decreased by the presence of a solute in solid solution. The solid solution has less capacity for cold deformation than the pure solvent metal, and is hardened more by a given amount of cold deformation. With similar methods of working, Alpha brass, for example, will not stand as much reduction as pure copper and, for a given amount of cold reduction, its hardness is increased more than that of copper.

Ductility of Solid Solutions.—Ductility is a property which is complex, in that it depends upon both plasticity and strength,

¹ "The Hardness of Certain Copper Alpha Solid Solutions," Institute of Metals, March meeting, 1923.

and one for which there is no single standard of measurement. While it can be said definitely that the addition to a metal of an element which enters into solid solution in it increases its hardness and decreases its plasticity, no such generalization can be made with regard to ductility.

If ductility is considered to be measured by the total reduction in the section of a wire which can be effected by drawing without annealing, then, in general, solid solutions are less ductile than the pure solvent metals. If the extent of the reduction which can be effected in a single die is considered as a measure, then in some cases the ductility of the solid solution is greater than that of the pure solvent.

It is often found that the addition of a solute to a metal increases its ductility, as measured by the elongation in the tensile test. Aluminum, zinc, and tin all increase the elongation of copper. Since commercial copper contains copper oxide, and these elements all reduce copper oxide, it might be suspected that their effect on elongation is due to deoxidation of the copper. That this is not the case is shown by the fact that the maximum elongation is attained only after the addition of an amount of aluminum, zinc, or tin greatly in excess of that required for complete deoxidation.

The elongation of magnesium, in the form of extruded rod, is more than doubled by the presence in solid solution of 4 per cent of aluminum. A similar increase is found in sand castings. With higher percentages of aluminum the elongation decreases.

There does not appear to be any element, the addition of which to pure aluminum increases its elongation. The elongation is definitely reduced by the addition of most elements. For material in the form of rolled and annealed bars, zinc does not seem to reduce the elongation very much up to about 10 or 15 per cent. Further additions of zinc cause a definite decrease in elongation.

The reduction of area in the tensile test is generally less for the solid solution than for the solvent, even when the elongation of the solid solution is the greater. The solid solution alloys do not show as much tendency to draw out locally, or "neck," as do the pure metals.

A Temperature Analogy.—The effects of a solute on the mechanical properties of a metal are in many ways similar to the effects of a lowering of temperature. The addition of zinc,

tin, or aluminum to copper increases its hardness and strength, and the rate at which it is hardened by cold work. The elongation is increased but the reduction of area becomes less. All of these effects are produced in pure copper by lowering the temperature of test.

That this analogy is not complete is shown by a consideration of other physical properties. The electrical conductivity of copper is increased by lowering of temperature but decreased by the addition of a solute.

Theory of Hardness of Solid Solutions.—The factors influencing the hardness and strength of solid solution alloys have mostly been considered above in connection with solid solubility, density, tendency toward the formation of intermetallic compounds, and electrical conductivity. Naturally, the same factors which influence other properties of solid solutions affect the hardness, but all properties are affected in different degrees. For example, a certain mixture of nickel and copper will have about double the hardness of copper, but an electric resistivity about 30 times that of copper.

Since hardness may be regarded as resistance to permanent deformation, and since permanent deformation of crystalline metals takes place largely by the movement of crystal fragments along slip planes, it follows that increased hardness must be caused by increased resistance to slip, or slip interference. The discussion of the hardness of solid solution alloys thus resolves itself into one of the probable causes for increased slip interference. Bridgman postulated an imperfect fit of solute atoms in the lattice of the solvent metal, and a "certain amount of distortion in the final result." He regarded the increased slip interference as due to a sort of staggering of the atoms on the potential slip planes. Rosenhain¹ advanced as a general theory of the increased slip interference of solid solutions the hypothesis that solute atoms distort the lattice of the solvent metal and that the increased resistance to slip is due to this distortion.

Figures 91, 92, and 93 represent Rosenhain's conception of the action of a large solute atom on a "ductile" lattice and on a "brittle" one. In this case the solute atom is supposed to have less attraction for the solvent atoms than the latter have for one another. In the ductile lattice, according to Rosenhain, this

¹ "Hardness of Solid Solutions," *Proc. Royal Soc.*, London, A vol. 99, p. 192; *Chem. Met. Eng.*, vol. 25, p. 243, Aug. 10, 1921.

causes local distortion and in a brittle lattice, general distortion, as shown in Figs. 92 and 93. The supposed difference in the manner of distortion of the lattices of ductile and brittle metals seems improbable because the property of ductility is not evidenced until permanent deformation takes place, whereas the nature of the distortion must exist prior to any attempt to deform.

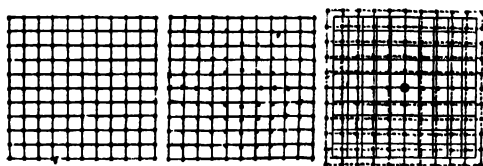


FIG. 91.

FIG. 92.

FIG. 93.

FIG. 91.—Spacing of atoms on principal plane of cubic lattice. (*Rosenhain.*)

FIG. 92.—Distortion in ductile lattice due to larger stranger atom. (*Rosenhain.*)

FIG. 93.—Distortion in stiff lattice due to large stranger atom. (*Rosenhain.*)

Furthermore, the solid solubility of the solute is regarded by Rosenhain as being dependent on the amount of lattice distortion—the greater the distortion the less the solid solubility.

The present authors¹ have regarded the increased resistance to slip as due partly to a greater attraction between unlike atoms of a solid solution than between like atoms, and partly to a general roughening of slip planes, due to the difference in size between solvent and solute atoms. The general statement may be made that when two elements form extensive solid solutions or inter-metallic compounds the attractive forces between the unlike atoms exceed those between the like atoms, since otherwise neither extensive solution nor combination would take place. That there should be distortion of the solvent lattice, due to the presence of solute atoms, seems logical. That such distortion, especially if it is the result of relatively high attractive forces between the unlike atoms, should increase slip interference seems certain.

The idea should not be accepted too eagerly, however, that any kind of distortion of the solvent lattice necessarily increases hardness. The first step in the permanent deformation of a metal is the "distortion" of the lattice by applied stress. In fact, the lattice must distort in a certain manner before slip can take place. In Rosenhain's illustration, given in Fig. 92, the supposition that

¹ "Slip Interference Theory of the Hardening of Metals," *Chem. Met. Eng.*, vol. 24, p. 1057, June 15, 1921.

the solute atom has less attraction for solvent atoms than the latter have for each other might produce a condition of weakening along the planes on either side of the foreign atom, because part of the work required to produce slip in the lattice of the pure solvent metal would be accomplished by the foreign atom.

It was mentioned in connection with the discussion of electrical conductivity that atoms in solid solution might cause a "fixing" of some electrons, and that such "fixing" of some of the free electrons might contribute to the hardness. With the present knowledge of solid solutions there remain certain unexplainable results, which can be referred to the unknown nature of the bonds between the unlike atoms in the alloys. The hardness, as well as other properties, such as solid solubility, density, electrical conductivity, and, in fact, all properties of solid solution alloys, depend to a large extent on the sizes of the atoms and the as yet imperfectly understood property which has been called specific attraction between the unlike atoms.

Corrodibility of Solid Solutions.—Tammann¹ has conducted many tests on alloys of gold and copper and gold and silver with respect to their solubility in aqueous solutions. The alloys were tested with reagents which would dissolve the copper or silver but not the gold. If the alloys were tested in the condition as cast, there were no sharp limits of composition marking the end of corrosion attack. After heating for a prolonged period a little below the melting point, to homogenize, very definite composition limits marking the end of corrosion attack were found. These limits were termed "reactive limits."

Expressed in atomic per cents, the "reactive limits" were, according to the reagents used, 12.5, 25 and 50. If only 1 copper or silver atom is required to form a molecule of the product of corrosion with the reagent used, then a complete layer of gold atoms is required to protect the copper or silver from attack. Such protection can be obtained with 50 atoms per cent gold, a few surface atoms of copper or silver being attacked until planes of gold atoms in the various grains are exposed to the surface. With less than 50 atoms per cent gold, reaction may continue because a complete protective layer of gold atoms would not be available. If a reagent requiring 2 atoms of silver or copper is

¹ "The Reactive Limit of Chemical Reagents on Metallic Solid Solutions," in "Lehrbuch der Metallographie," p. 317, 1921.

used, then the amount of gold can be reduced to less than 50 atoms per cent—in fact, to 25 atoms per cent—and a protecting layer in which 2 copper or silver atoms are not neighboring will prevent further attack.

In order for these sharp limits to be manifest, the alloys must be homogenized, *i.e.*, heated for a long time near but below the melting point to allow the atoms to arrange themselves in equilibrium positions. Furthermore, in hot solutions, diffusion of copper or silver atoms may disturb the “reactive limit” by allowing these atoms to migrate to the reagent.

These tests give evidence that the atoms of the solute (gold) were, after homogenization, atomically dispersed in the solvents (silver or copper) and were distributed evenly when the space lattice permitted. This is as it should be according to the laws of ordinary solutions, namely, the solute tends to disperse itself as much as possible. The limit of dispersion in metallic solid solutions is reached when the atoms of the solute separate and are evenly distributed among the atoms of the solvent.

Solution Forces.—The tendency of different gases to diffuse into each other until a homogeneous mixture is produced is due to the energy of thermal agitation of the gas molecules. These molecules are in continuous motion and, naturally, become completely mixed unless there is some opposing force tending to segregate them. In the case of gases, gravitation acts as such a segregating force and there seems to be a slight segregation in the atmosphere of the earth, the heavier gases being somewhat concentrated near the surface of the earth.

The nature of the forces of attraction or repulsion between various kinds of molecules must also be considered. The attractive forces between molecules of oxygen are very low, as shown by the low boiling point of oxygen. The attraction of nitrogen molecules for each other is likewise very low. It is possible that the attraction of a nitrogen molecule for an oxygen molecule is greater and that this attraction assists in making the earth's atmosphere uniform. On the other hand, the attraction of nitrogen molecules for each other may be greater than the attraction of nitrogen molecules for oxygen molecules. If this is the case, then the attractive forces between the nitrogen molecules tend to produce segregation rather than homogeneity. Such a condition would act like gravitation in opposing the diffusion tendencies of the gases due to thermal agitation.

Liquid solubilities as well as gaseous solubilities depend, in part, on the thermal energy of the atoms or molecules. Consider, for example, the relations of molten copper and molten lead. These metals do not mix completely in the liquid state, but form two separate layers, one rich in copper and the other rich in lead. As the temperature of such a mixture is raised, the lead-rich liquid becomes richer in copper, and the copper-rich liquid becomes richer in lead; that is, the solubility of each metal in the other increases with rising temperature.

It is evident that there is very little attraction between copper atoms and lead atoms. If the attraction of copper atoms for each other or of lead atoms for each other exceeds that of copper atoms for lead atoms, then the tendency is for the copper and lead to segregate rather than mix. The extent to which they do mix is probably due largely to the thermal motion of their atoms. This force is opposed by the nature of the specific attractions between the atoms but, as the temperature is raised, the thermal energy of the atoms becomes more and more predominant and increased solubility is the result. It is to be considered that there is a constant interchange of atoms from one liquid layer to the other and that the observed solubilities represent a condition of mobile equilibrium.

The importance of thermal energy as a force tending to produce solution is naturally less in the case of liquids than in the case of gases, because the phenomenon of liquefaction itself represents the predominance of the attractive forces between the atoms or molecules of the substance over the kinetic energy of these particles. In solid solutions, thermal energy must still be considered as a factor, although probably of even less importance than in liquid solutions. In the case of liquid copper and liquid lead, the atoms of each element are free to penetrate into masses of the other element. When these metals have solidified, this freedom disappears to a large extent because the atoms of each metal become fixed in comparatively rigid crystalline structures. Atomic volume then becomes an important consideration in determining whether an atom can penetrate a crystal. For any given relation between atomic volumes, diffusion must be easier the higher the temperature, because at the higher temperatures the structure of a crystal is less rigidly fixed than at low temperatures.

Granted a suitable relation between the atomic volumes of the elements concerned and a sufficient temperature to produce the required thermal agitation, the process of solution in the solid state must depend largely on the specific attractive forces between the atoms. If intimate contact is established between two metals which have similar atomic volumes and types of space lattice, no very extended solution can take place unless the attraction between the unlike atoms is greater than that between like atoms.

A high degree of attraction or affinity between the atoms of different elements is favorable to the formation of strong chemical compounds rather than of solid solutions. Three degrees of affinity may therefore be distinguished roughly as follows:

1. Affinity too small to produce either solution or chemical combination.

2. A moderate degree of affinity, such as to encourage solubility when other conditions are suitable but not sufficient to cause chemical combination.

3. A high degree of affinity favorable to the formation of definite compounds, and unfavorable to the formation of extended solid solutions.

Atomic Volume vs. Diffusion.—Interesting illustrations of the bearing of atomic volume on diffusion are found in the behavior of carbon, phosphorus, and hydrogen in steel. Carbon having a very low atomic volume diffuses quite readily in iron, even at temperatures as low as 300° C., although diffusion is very much more rapid at higher temperatures, especially after the Gamma variety of iron becomes the stable form. Phosphorus has an atomic volume much larger than that of iron and diffuses only with great difficulty, although it forms solid solutions to quite an appreciable extent. The phosphorus in solid solution in iron is segregated as a result of the process of solidification, and this segregation can be removed by diffusion only by prolonged heating at very high temperatures.

At ordinary temperatures hydrogen gas does not penetrate iron or steel. Hydrogen can be kept in steel containers under very high pressure without leakage. At a red heat, however, hydrogen diffuses quite readily through iron, presumably because of the opening up of the iron space lattice and the decreased rigidity of the crystalline structure. At both low and high temperatures it is the hydrogen molecule which must penetrate

the iron. If hydrogen is produced in contact with iron in a nascent or atomic condition, it readily penetrates the iron, even at room temperature. A familiar example of this is found in the embrittlement of steel by acid pickling, due to the absorption of hydrogen. The small size of the hydrogen atom as compared with the hydrogen molecule accounts for the fact that nascent hydrogen can penetrate iron at temperatures at which molecular hydrogen cannot.

From recent work it seems that the red hardness of high-speed steels is largely due to the stability of small particles of hard tungsten compounds. This stability seems to depend on the large atomic volume of tungsten, which prevents it from diffusing in iron, even at fairly high temperatures.

Diffusion of "Insoluble" Compounds.—Many substances, especially intermetallic compounds and some of the compounds of metals with the non-metallic elements, possess very small solid solubilities, but still show marked evidence of a solubility sufficient to allow diffusion. The solubility of iron carbide in Alpha iron is at no temperature greater than about 0.10 per cent carbon. Nevertheless, marked changes in the shape and size of carbide particles can be brought about by heating at temperatures in the neighborhood of 700° C. These changes are in the direction of larger size and more compact shape of the particles, and are due to the forces which are responsible for grain growth in general and which have been discussed in Chap. V. The accomplishment of this result depends upon the diffusion of carbon through the iron.

Similar changes have been observed in the shape and size of particles of copper oxide in copper and of thoria in tungsten. Both of these compounds are ordinarily considered to be practically insoluble, but their solubility is sufficient for some diffusion to take place. This does not mean, of course, that the compound diffuses as such, but merely that its constituent elements diffuse, probably in the form of separate atoms.

The original particle size of these compounds is very important in determining the rate at which this process takes place. Starting with a material containing relatively large particles, the change may not be observed, whereas the same material containing particles of very small size would quickly show a change on heating at the proper temperature. It is possible that there are no compounds found in metals which would not show such

diffusion if present in sufficiently small particles and if subjected to the proper temperatures.

The growth of thoria particles in tungsten is illustrated in Figs. 94 and 95, which show the sizes of these particles in the cold and hot portions of a tungsten ingot.

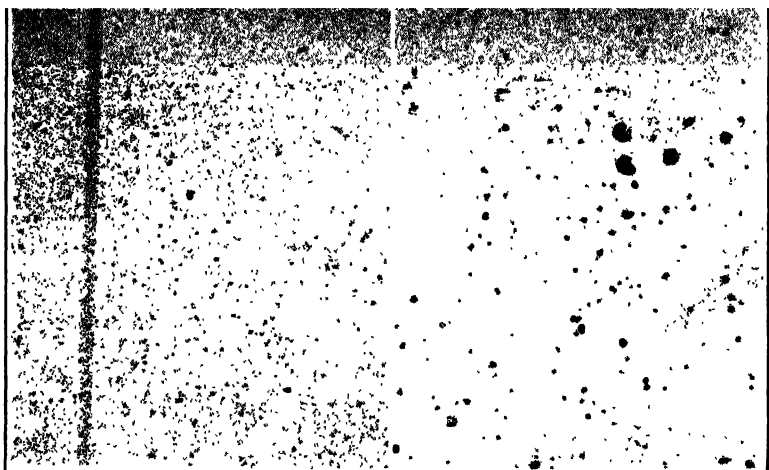


FIG. 94.—Thoria particles near cold end of tungsten ingot.

FIG. 95.—Thoria particles in hot portion of tungsten ingot.

Molecules in Solid Solutions.—Until recently it was customary, though not at all universal, to consider that compounds of metals dissolve “as such” in the solid solvent. The iron-carbon solid solution, austenite, for example, is usually spoken of as a solution of iron carbide or cementite in iron, and it was formerly the general view that the carbon in this solution was in the form of carbide molecules. This view now seems highly improbable in the light of new knowledge of the constitution of solids and the internal structure of metals.

Most of the compounds of metals which are found in alloys seem to occur only in the solid crystalline state, and there is no evidence of the existence of any definite unit of such substances which can be called a molecule.

Even granting that compound molecules may exist, they would be too large to diffuse through the rigid space lattice of the solvent metal. Carbon readily diffuses through iron, but can scarcely do so in the form of molecules of iron carbide (empirical formula, Fe_3C), which would have to contain at least 3 atoms of iron and 1

of carbon. The carbon atoms alone must be the ones which diffuse.

The view has been advanced that these migrating carbon atoms link up in each position with the neighboring iron atoms, to form what are practically molecules of carbide. It seems to the present authors that a group of atoms cannot properly be called a molecule unless it participates as a unit in such physical changes as diffusion, solution, and precipitation.

The solutions of carbon in iron have been mentioned merely as an example, and similar considerations apply in the case of solid solutions of other compounds in metals, such as of CuAl_2 in aluminum or Cu_3P in copper. In all cases, the atom appears to be the physical unit of the solute. From this conception it follows that the process of precipitation of a compound from metallic solid solution is one of *formation*, while the solution of a compound involves *dissociation*.

Conditions Determining Solid Solubility.—There are listed in Table XVII the better known binary combinations of metals which dissolve in each other in the solid state in all proportions. The table also gives the atomic weights, atomic volumes, crystal structures, and melting points. The notation "Min." in the column headed "Remarks" indicates that the freezing point curve of the alloy series passes through a minimum.

From a consideration of the data given in this table some general conclusions can be formed regarding the factors which govern solid solubilities.

In 16 of the 23 systems given, both elements crystallize with the same type of space lattice. While it might appear that lead and indium have decidedly different lattice types, as a matter of fact, if one of its three axes were shortened 6 per cent, the indium lattice would be face-centered cubic. The lattice type of manganese is not known. Such x-ray crystallograms as have been taken suggest that it does not crystallize with either a face-centered or body-centered cubic lattice. The systems Ni-Cr and Co-Cr are known to form unbroken series of solid solutions, and chromium is known to crystallize with a body-centered cubic lattice and nickel and cobalt with face-centered cubic lattices. It thus appears that similar types of crystal lattice of the elements favor, but are not necessary for, mutual solubility. The distinction is that when the lattices of the constituent elements are of the same type there is a continuous

TABLE XVII.—ALLOY SYSTEMS CONSISTING OF COMPLETE SERIES OF SOLID SOLUTIONS

Components	Atomic weight	Atomic volume	Crystal structure	Melting point	Remarks
Bismuth.	208.00	21.20	Rhombohedral	271.0	
Antimony	120.20	18.00	Rhombohedral	630.0	
Cobalt.	58.97	6.80	Face-centered cubic	1,480.0	
Chromium.	52.00	7.50	Body-centered cubic	1,615.0	Min.
Cobalt	58.97	6.80	Face-centered cubic	1,480.0	
Manganese	54.93	7.40	Not known	1,230.0	Min.
Copper	63.57	7.15	Face-centered cubic	1,083.0	
Gold	197.20	10.20	Face-centered cubic	1,063.0	Min.
Copper	63.57	7.15	Face-centered cubic	1,083.0	
Manganese	54.93	7.40	Not known	1,230.0	Min.
Copper	63.57	7.15	Face-centered cubic	1,083.0	
Nickel	58.68	6.70	Face-centered cubic	1,452.0	
Copper	63.57	7.15	Face-centered cubic	1,083.0	
Palladium	106.70	8.80	Face-centered cubic	1,550.0	
Copper	63.57	7.15	Face-centered cubic	1,083.0	
Platinum	195.20	9.20	Face-centered cubic	1,755.0	
Gold	197.20	10.20	Face-centered cubic	1,063.0	
Palladium	106.70	8.80	Face-centered cubic	1,550.0	
Gold	197.20	10.20	Face-centered cubic	1,063.0	
Platinum	195.20	9.20	Face-centered cubic	1,755.0	
Iron	55.84	7.10	Face-centered cubic	1,530.0	Gamma iron
Cobalt.	58.97	6.80	Face-centered cubic	1,480.0	
Iron	55.84	7.10	Face-centered cubic	1,530.0	Gamma iron
Manganese	54.93	7.40	Not known	1,230.0	
Iron	55.84	7.10	Face-centered cubic	1,530.0	Gamma iron
Nickel	58.68	6.70	Face-centered cubic	1,452.0	Slight min.
Iron	55.84	7.10	Face-centered cubic	1,530.0	Gamma iron
Platinum	195.20	9.20	Face-centered cubic	1,755.0	
Lead	207.20	18.30	Face-centered cubic	327.4	
Indium	114.80	15.70	Face-centered tetragonal	155.0	
Magnesium	24.32	14.00	Hexagonal, close-packed	650.0	
Cadmium	112.40	13.00	Hexagonal, close-packed	321.0	
Nickel	58.68	6.70	Face-centered cubic	1,452.0	
Chromium	52.00	7.50	Body-centered cubic	1,615.0	Min.
Nickel	58.68	6.70	Face-centered cubic	1,452.0	
Cobalt	58.97	6.80	Face-centered cubic	1,480.0	
Nickel	58.68	6.70	Face-centered cubic	1,452.0	
Manganese	54.93	7.40	Not known	1,230.0	Min.
Nickel	58.68	6.70	Face-centered cubic	1,452.0	
Palladium	106.70	8.80	Face-centered cubic	1,550.0	Min.
Silver	107.88	10.20	Face-centered cubic	960.5	
Gold.	197.20	10.20	Face-centered cubic	1,063.0	
Silver	107.88	10.20	Face-centered cubic	960.5	
Palladium	106.70	8.80	Face-centered cubic	1,550.0	
Tungsten	184.00	9.60	Body-centered cubic	3,400.0	
Molybdenum	96.00	9.60	Body-centered cubic	2,550.0	

change in the lattices of the alloys with progressive change in composition (Fig. 88), whereas when the lattices of the constituent elements are of a different type there is a discontinuity in lattice type and there may exist within a certain range of composition both types of lattice simultaneously, as shown in Fig. 87. It will be noted that, in those solid solution alloy systems in which the constituent elements crystallize with different types of lattice, the atomic volumes of the constituent elements are very nearly the same.

In fact, the atomic volumes of metals seem to be very important in determining the degree of solid solubility. The system in Table XVII showing the greatest difference between the atomic volumes of the constituent elements is copper-gold. These elements crystallize with the same type of lattice and their melting points are only 20° C. apart. The atomic volume of a metal is the value obtained by dividing the atomic weight by the density at ordinary temperature. The number obtained is a relative measure of the volume dominated by each atom under the conditions of *mutual attraction of the like atoms*. It does not follow that the atom has a fixed volume, and if of proper size will always be capable of substituting for atoms of another metal of a similar size. For example, silver and aluminum have approximately the same atomic volume and the same type of space lattice, yet they do not form a complete series of solid solutions. The attractive force or affinity between aluminum and silver atoms is such as to cause intermetallic compounds to form. There is also quite a disparity in the melting points of aluminum and silver. Again, the atomic volumes of lead and antimony are about the same, but these metals do not form solid solutions. The crystal structures of these elements are different.

Other things being similar, it seems that disparity in melting points is unfavorable to the formation of an unbroken series of solid solutions. The melting point itself may only be a sign, but the factors which determine melting point also affect solid solubility.

Consider, for example, the binary systems of the elements, Ni, Cu, Ag, and Au. Ni-Cu, Au-Cu, and Ag-Au form unbroken series of solid solutions. Ni-Au and Cu-Ag form eutectic series with limited solid solutions. Ni-Ag form a system showing incomplete solubility, even in the liquid state.

TABLE XVIII.—SOME PROPERTIES OF NICKEL, COPPER, SILVER, AND GOLD AFFECTING SOLUBILITY

Metal	Atomic volume	Melting point, degrees Centigrade	Crystal structure
Nickel.....	6.70	1,452.0	Face-centered cubic
Copper.....	7.15	1,083.0	Face-centered cubic
Silver.....	10.20	960.5	Face-centered cubic
Gold.....	10.20	1,063.0	Face-centered cubic

The more important properties of these elements governing solid solubility are given in Table XVIII. All of these metals crystallize with the same type of lattice which is favorable for the formation of unbroken series of solid solutions. Copper and nickel have very similar atomic volumes, so it is not surprising that solid solutions form. Gold and silver form continuous solid solutions and have practically the same atomic volume. Silver and nickel show the greatest difference in melting point and equal disparity with gold and nickel in atomic volume. Ni-Ag depart most from a complete solid solution series. Although Au-Cu form an unbroken series of solid solutions, the freezing point passes through a minimum, just as if a eutectic would form but was prevented from forming because the solubility limit extends up to the hypothetical eutectic composition. There is quite a disparity between the atomic volumes of gold and copper, but the melting points are very close together. There is the same difference between the atomic volumes of silver and copper as between gold and copper. There is a greater difference in melting point. Ag-Cu form a eutectiferous series.

It is interesting to call attention to these observations, but it must be borne in mind that no accurate prediction as to the degree of solubility of unknown alloys can be made with all of the present knowledge. The unknown property which might be called the "specific attraction between unlike atoms," will prove all-important in interpreting not only the solid solubility but also many other properties of alloys. Low specific attraction between unlike atoms is conducive to insolubility in the solid state and in extreme cases insolubility in the liquid state. A specific attraction between unlike atoms moderately greater than between like atoms is conducive, other things being favorable, to the

formation of unbroken series of solid solutions. High specific attraction between unlike atoms is conducive to the formation of intermetallic compounds.

To sum up, the more important factors favoring the formation of complete series of solid solutions in binary alloys are:

1. Similar atomic volumes of the constituent elements.
2. Similar crystalline structure of the constituent elements.
3. Attraction between unlike atoms moderately greater than between like atoms.
4. Similar melting points of the constituent elements.

CHAPTER IX

CONSTITUTION OF ALLOYS

Most alloys are aggregates, in that they are made up structurally of two or more physically different constituents. The properties of an alloy, or aggregate, are determined by the quantities of the various constituents, their distribution, their specific properties, and, to a smaller extent, by the surface forces between them. A rational understanding of the properties of alloys therefore requires a knowledge of alloy constitution; that is, of what constituents are present under various circumstances, and in what proportions.

The problem of alloy constitution is complicated by the fact that under ordinary conditions alloys are often not in a state of physicochemical equilibrium. The internal changes which must take place to establish equilibrium proceed slowly because of the rigidity of the solid state, and at low temperatures may be entirely arrested, so that an unstable structure becomes, for all practical purposes, a stable and permanent one.

It is nevertheless necessary to base the study of constitution on conditions of true equilibrium. It is only under such conditions that the constitution of an alloy is *definite*. The equilibrium condition is the condition which is approached as a limit when opportunity for atomic rearrangement is given by slow cooling or prolonged annealing. It is the standard from which actual conditions are to be considered as departures of variable and indefinite extent.

The study of physicochemical equilibria involves the use of a somewhat special phraseology, including a few words whose meanings in this connection must be thoroughly understood.

System.—A *system* is a substance or group of substances selected for study, considered as “isolated” from its surroundings, in the sense that it is held to be free from the interference of extraneous bodies. If the alloys of copper and nickel, for example, are being investigated the whole group is spoken of as the “copper-nickel system.” The system includes all alloys from

pure copper to pure nickel, but does not include other substances incidentally present, such as the material of a containing crucible, or a gaseous atmosphere in contact with the alloy. If, in the case of a particular alloy of copper and nickel, it is said that the system is in a state of equilibrium, it is meant that the alloy is in a state of internal equilibrium, and not that it is in equilibrium with the material of its container or other substances with which it is incidentally in contact. The material of the container may react with the alloys and exert an important influence on their constitution. If it is desired that such a reaction be allowed to go to completion and its effect on the alloys be considered, the reacting material must be included in the system. Thus, there might be a copper-nickel-carbon system or, considering the effects of an air atmosphere rather than a container, a copper-nickel-oxygen system. Usually, it is undesirable to consider extraneous substances, and it is assumed that sufficient precautions are taken to exclude the effects of any materials not mentioned in describing the system.

Phase.—Each physically distinct, homogeneous part of a system is called a *phase*. At the freezing point of a metal two phases—solid and liquid—are present. The process of freezing is a phase change. A phase must be physically and chemically homogeneous, but need not be chemically simple. A gaseous mixture or a solution may form a phase. In alloys, the important phases are liquid solutions, solid metals or metalloids, metallic solid solutions, and chemical compounds. There can never be more than one gaseous phase in a system, because all gases are mutually soluble in all proportions to form homogeneous mixtures. In the case of liquid and solid phases the number is indefinite, increasing, in general, with the number of participating substances.

Equilibrium.—Equilibrium is a condition of balanced forces, so that the resultant is zero and the condition appears one of rest rather than of change. No measured quantity alters with time. Consider, for example, the system, *water-sodium chloride*, at a temperature of 30° C. Suppose 500 gr. of anhydrous salt are added to 1,000 c.c. of water. If the concentration of salt in the water is determined from time to time, it will be found to increase until a value of 36 gr. per 100 gr. of water is reached, beyond which no further change will be observed. The solution is then said to be in equilibrium with the solid salt.

Modern conceptions view equilibrium as a kinetic rather than a static condition. Instead of considering that all change ceases when the salt solution becomes saturated, it is considered that there is a continual dissolving of salt on the one hand, and a continual precipitation on the other, the two processes going on at exactly equal rates so that no change is observed. If some water is placed in an enclosed vessel, there is at each temperature a definite pressure of water vapor in the space above the water. After a time the system comes to equilibrium, when it is to be considered that there are constant processes of evaporation and condensation, the number of molecules leaving the liquid in a given time to form vapor being exactly equal to the number of molecules condensing to form liquid.

A condition of true rest or freedom from change is liable to be one of false rather than real equilibrium. The chief criterion of true equilibrium is that the same condition of equilibrium is reached from whichever side it is approached. Thus, in the case of the salt solution, the same concentration is reached no matter whether one starts with water and adds salt, or starts with a supersaturated solution (obtained by heating to a higher temperature) and allows solid to crystallize out. Or in case of the system, *water-water vapor*, the same vapor pressure will be obtained when the water is heated up to the given temperature as when it is cooled down from a higher temperature. These are cases of *real* equilibrium.

Consider water in contact with a mixture of hydrogen and oxygen at ordinary temperatures. The condition is stable in that it can be maintained indefinitely without measurable change. If the temperature is raised beyond a certain limit, there is a sudden change, and the system no longer regains its original condition on cooling to ordinary temperatures. The equilibrium was therefore only apparent.

Equilibrium existing in one phase is called homogeneous, and equilibrium existing between two or more phases is called heterogeneous. The study of alloy constitution is concerned with heterogeneous equilibria.

A distinction is sometimes drawn between physical and chemical equilibria, considering equilibria existing between various physical states or conditions of aggregation, as between ice, water, and water vapor, as physical, and equilibria between substances and the products of their reaction as chemical. In

the case of phase changes in alloys it is often difficult to say whether the change is physical or chemical, and the distinction has no significance.

Equilibria can be more usefully classified for our present purpose into (1) phasial equilibria, and (2) structural equilibria. Complete structural equilibrium is rarely, if ever, attained in metals and alloys. It has been pointed out in Chap. V that the stable or equilibrium form of a solid metal is a single crystal. In an alloy containing several phases, structural equilibrium would generally be attained only when each phase formed one continuous portion of the aggregate. There is a tendency to approach such a condition whenever opportunity for atomic rearrangement is afforded. It should not be forgotten, however, that a structural condition may be reached which is practically permanent up to certain temperatures, although it is not the most stable condition possible. Refer, in this connection, to the discussion of "equilibrium grain size" in Chap. V.

In many cases when conditions of stable equilibrium require the appearance of a new phase, there is a reluctance in the appearance of this phase which leads to a condition of *metastable* equilibrium. It has long been known, for example, that, in the absence of any trace of solid ice, water can be undercooled without the occurrence of freezing. As long as no ice is introduced into the system and there is no undue mechanical agitation, the water may be maintained in the liquid form indefinitely at temperatures below its true freezing point. The vapor pressure of water in this region has been investigated, and it has been found that the vapor pressure curve is a continuation of the normal curve for temperatures above 0°C . The undercooled water is in equilibrium with its vapor, but the equilibrium is metastable. The introduction of a small crystal of ice into the system precipitates freezing, whereupon the latent heat of fusion raises the temperature of the system to the true freezing point.

Many metals in the liquid state commonly cool to temperatures slightly below the true freezing point before freezing begins. The appearance of new phases in the solid state is subject to still greater retardation. An important case occurs in the iron-carbon system. In ordinary steels, the phase which is stable at temperatures in the hardening range (about 770°C . for a tool steel) normally undergoes decomposition on slow cooling at about 690°C . By quenching, however, this phase can be

retained down to about $300^{\circ}\text{C}.$, when it undergoes very suddenly the change which under conditions of equilibrium should have taken place at about $700^{\circ}\text{C}.$ This suppression is probably the chief factor in the hardening of steel.

Liquids can often be heated above their boiling points without the appearance of the vapor phase. The overheating, and hence "bumping," of water heated in a glass flask is commonly observed, especially when it contains a little alkali, which cleans the surface of the glass. Water globules suspended in oil of the same specific gravity have been heated as high as $145^{\circ}\text{C}.$ without vaporizing. The presence of a trace of the vapor phase prevents such overheating. Conversely, an atmosphere containing water vapor can be cooled below the dew point without the appearance of fog, if no dust or other particles are present to act as nuclei. It has not so far been found possible, however, to overheat a solid without fusion taking place.

The most stable condition is always a condition of minimum energy content. The change from metastable equilibrium to stable equilibrium always evolves energy, usually in the form of heat. Metastable phases possess higher vapor pressures and higher solubilities in solvents than do stable phases under the same conditions. Thus, at temperatures below $0^{\circ}\text{C}.$ the vapor pressure of water is higher than that of the solid phase, ice. The solubility of iron carbide in iron is at all temperatures greater than that of graphitic carbon.

Component.—The components of a system are the chemical elements or compounds which participate in the equilibria. Whenever all the phases have the same chemical composition, there is only one component, and the system is classified as a one-component system. The equilibria between water, water vapor, and ice are those of the one-component system, *water*. The vaporization, melting, and allotropic transformation of pure metals are phase changes in one-component systems.

In systems of more than one component there is sometimes difficulty in naming the components, although this is rarely the case with alloys. Whenever an alloy system includes all of the alloys formed by two elements, then those two elements are the components. Thus, in considering all of the alloys formed by copper and nickel, the components are copper and nickel. If there is being considered only a part of a two-component, or binary, system, in which a chemical compound occurs, then that

compound may be regarded as one of the components. In the metastable iron-carbon system, for example, interest is confined to that part of the system containing less carbon than the iron carbide, cementite (Fe_3C). The components may then be considered as iron and cementite, instead of iron and carbon.

Alloy systems containing three or more elements offer more possibilities for confusion. This may be illustrated by alloys composed of aluminum, magnesium, and silicon. If all the possible alloys formed by these elements are considered, then each element is a component and the system is a three-component, or ternary, system. A very important class of alloys, however, are those in which magnesium and silicon are present in substantially the proportions required to form the compound, Mg_2Si . With this restriction, the system becomes a binary system in which the two components are aluminum and magnesium silicide. .

Further difficulties which may be encountered in selecting the components of non-metallic systems need not be discussed here. A general rule may be given, applicable to all cases (Findlay).¹

As the components of a system there are to be chosen the *smallest number* of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.

Variability.—In the study of phase equilibria, a system is generally regarded as possessing only three independently variable factors—temperature, pressure, and the concentration (or volume) of the components of the system. The number of these factors which must be fixed in order to define the condition of a system depends, for any given system, upon the number of phases present. This may be illustrated by a consideration of the system, *water*.

When only one phase is present, two of the variable factors must be fixed in order to define the condition of the system. Consider a given mass of the gas phase, water vapor, and suppose the temperature to be arbitrarily fixed. The condition of the system is not defined, since the vapor may occupy several different volumes and exist under different pressures. At any fixed pressure, the temperature and volume may vary. Similarly,

¹ FINDLAY, ALEX., "The Phase Rule," Longmans, Green & Co.

while the vapor occupies a given fixed volume (the concentration, therefore, being fixed), both temperature and pressure may be changed. If, however, two of the variables are arbitrarily fixed, then the third is thereby automatically fixed. If the temperature and pressure are fixed, for example, a given mass of water vapor can occupy only one volume. When two variables must be fixed to define the condition of the system, the system is said to possess *two degrees of freedom*, or to be *bivariant*.

If two phases of this system are present, such as liquid water and water vapor, then the condition of the system is defined by fixing one variable. The system possesses *one degree of freedom*, or is *monovariant*. If the temperature is fixed, then the pressure is also determined. At a given temperature, water and vapor can coexist only at a definite pressure.

When the three phases, ice, water, and vapor, are all present together, the system is *invariant*, or *non-variant*. These three phases can coexist only at one definite temperature and pressure of the vapor. None of the variables can be changed without causing the disappearance of one of the phases.

In general, the number of degrees of freedom of a system may be defined as the "number of the variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined" (Findlay).

The Laws of Equilibria.—There are two important general laws of equilibria, the phase rule of Willard Gibbs, and the general theorem of Le Chatelier.

The phase rule expresses definite numerical relations between the number of components in a system, the number of coexisting phases in equilibrium and the number of degrees of freedom:

In a system consisting of C components the greatest number of phases that can be simultaneously present in a state of equilibrium is $C + 2$, and when $C + 2$ phases are present, the system is invariant. The temperature, pressure, and concentration have fixed values.

If there are C components and $C + 1$ phases, the system is univariant.

With C components and C phases, the system is bivariant.

This law may be conveniently expressed in the form of the equation

$$F = C + 2 - P,$$

where F is the number of degrees of freedom, C the number of components, and P the number of phases.

In the study of metals and alloys, pressure is ordinarily omitted as a variable, because it is substantially constant (atmospheric) throughout most operations, and because the volume changes in the liquid and solid states are so small that the influence of pressure is negligible. The elimination of one variable automatically eliminates one degree of freedom, so the equation of the phase rule may be rewritten, for systems under constant pressure,

$$F = C + 1 - P.$$

While the phase rule applies to systems in a state of equilibrium, the theorem of Le Chatelier applies to the changes that take place when equilibrium is upset by alteration of the external conditions, temperature and pressure. The theorem may be stated as follows (Ostwald, translated by Findlay):

If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, *i.e.*, one by which its effect is partially destroyed.

The application of this general theorem becomes apparent on the statement of two special cases covering the effects of alterations in pressure and temperature respectively.

When a system in equilibrium is subjected to an increase in pressure, that reaction takes place which is accompanied by a decrease in volume; if the pressure on the system is decreased, a reaction takes place which is accompanied by an increase in volume.

When the temperature of a system in equilibrium is raised, that reaction takes place which involves an absorption of heat; when the temperature is lowered, that reaction occurs which is accompanied by an evolution of heat.

Phase Changes in Pure Metals.—A pure metal constitutes a one-component system, in which there occur one vapor phase, one liquid phase, and one or more solid phases. Some of the metals exist in a number of solid allotropic forms, distinguished from each other by different arrangements of atoms in the crystal. In a metallic solid solution, the atoms of the solvent metal are usually replaced by those of the solute and only one crystal form or space lattice is preserved. The various allotropic

modifications of a metal cannot, therefore, be "soluble" in each other, but must form separate phases.

When all three variables are considered, the equation of the phase rule, $F = C + 2 - P$, becomes, for a pure metal, $F = 3 - P$. The system becomes invariant when three phases are present. This occurs at the *triple point*, where solid, liquid, and vapor are in equilibrium at a fixed temperature and a fixed pressure. When only two phases are present in equilibrium,

$$F = 3 - 2 = 1,$$

the system is univariant or has one degree of freedom. Thus when vapor and liquid or vapor and solid are present together, if the temperature is arbitrarily fixed, then the pressure is determined;

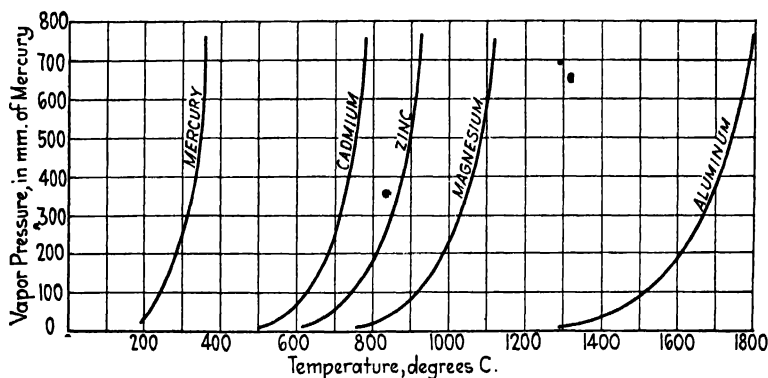


FIG. 96.—Vapor pressure curves of various metals.

or if the pressure is arbitrarily selected, then the temperature is fixed. In other words, the vapor pressure of a metal is definite at each temperature. The boiling point is the temperature at which the vapor pressure is equal to the external pressure, normal atmospheric pressure being 760 mm. of mercury. The boiling point is thus a fixed and definite temperature.

In Fig. 96 are shown vapor pressure curves of several metals.

All metals can be vaporized at sufficiently high temperatures, the most refractory metal, tungsten, boiling at about 6,000° C. Mercury and zinc, which boil at relatively low temperatures, are produced commercially by processes involving distillation. Many metals have been distilled experimentally under ordinary atmospheric pressures.

The figures show that the vaporization of metals is greatly facilitated by reduced pressure. The darkening of the bulbs of evacuated electric lamps by the deposition of metallic tungsten vaporized from the filament is a regular occurrence.

The "sherardizing" process for zinc-coating iron and steel depends on the vaporization of zinc at a temperature where the vapor pressure is very low. A similar process, called "calorizing," consists in coating iron and steel articles with a layer rich in aluminum, by heating in a mixture containing finely divided aluminum and aluminum oxide at about 900° C. In these processes the zinc and aluminum reach the iron by vaporization.

The system is also univariant when the two phases in equilibrium are solid and liquid. The temperature at which solid and liquid are in equilibrium with each other is the melting point, or freezing point, of the metal, and is fixed and definite for each value of pressure. The effect of pressure on the melting point can be predicted from the law of Le Chatelier given above. Normally, metals expand on melting, and the effect of an increase in pressure is to raise the melting point. The principal exception to this rule is bismuth, which contracts on melting and whose melting point is lowered by increased pressure. The volume changes in the metals on melting and freezing are relatively small, and the melting point is not appreciably affected by pressures ordinarily encountered. For this reason, it is usual to omit the pressure variable from consideration. The phase rule equation for the condensed system is then

$$F = C + 1 - P \text{ or } F = 2 - P,$$

which becomes

$$F = 2 - 2 = 0$$

when solid and liquid are present together. The melting point is therefore regarded as a constant of the metal, atmospheric pressure being understood.

Similar conditions hold in the transformation of one solid allotrope to another. Two phases are present and, if the pressure factor is considered, the system is univariant, the temperature of the transformation varying with the pressure. Again, the volume changes are small and the effect of ordinary pressures can be neglected. The system then becomes invariant, and the temperature of the allotropic transformation is a fixed and definite temperature, like the melting point.

Under constant pressure and conditions of equilibrium all of the phase changes in pure metals take place at definite, characteristic temperatures. Each phase has a definite temperature range of stable existence. Consider tin, for example, at atmospheric pressure. Above $2,200^{\circ}\text{C}$. the stable phase is the vapor; between $2,200^{\circ}\text{C}$. and 232°C . the stable phase is the liquid; at 232°C . the metal solidifies and ordinary white tin (body-centered tetragonal) is the stable phase down to 18°C .; at this temperature there may be a transformation to the allotropic form, gray tin (tetrahedral cubic), which is the stable phase below 18°C . Ordinary changes in pressure affect the temperature of transformation of the vapor to the liquid or solid phase to an important extent. The effect of ordinary changes of pressure on the melting point or temperature of allotropic transformation is slight.

The various phases of a metal have different energy contents. Thus the vapor phase possesses more energy than the liquid by an amount represented, at the boiling point, by the latent heat of evaporation, and the liquid phase possesses more energy than the solid by an amount equal, at the melting point, to the latent heat of fusion. There is also a difference in the energy contents of various allotropic modifications. In accordance with the law of Le Chatelier, the phases stable at the higher temperatures have the greater energy content. Phase changes that take place on cooling are always accompanied by an evolution of heat, while the reverse changes on heating always involve heat absorption.

Cooling Curves.—The energy changes which accompany phase changes on heating and cooling furnish the most commonly observed indications of the temperatures at which such changes occur. If a mass of molten metal is allowed to cool undisturbed, there is a marked arrest in the rate of cooling when the metal begins to solidify, due to the liberation of the latent heat of fusion.

As long as solidification is taking place in a pure metal, the temperature remains constant, since two phases are present and (pressure being assumed constant) the system is invariant. When the last of the liquid is frozen, cooling is resumed at a rate comparable to that which obtained before the freezing began.

This process can be represented graphically by plotting temperature and time data taken during the cooling. There are several ways of taking such observations and of plotting them,

resulting in corresponding types of cooling curves. Of these the type known as the *time-temperature* curve is probably the most easily understood and the most useful for illustrative purposes. In this curve the temperature of the cooling metal is plotted against the total time elapsed from the beginning of the observed cooling. The taking of observations usually consists in noting the temperature after the lapse of certain equal intervals of time, say, every 20 sec. The observed temperatures are then plotted against total time.

A typical time-temperature cooling curve of a pure metal is shown in Fig. 97. The first portion, *AB*, represents undisturbed cooling of the molten metal, at a rate which gradually decreases as the temperature is lowered, because of decreased rate of heat loss to the surroundings. At *B* solidification begins, and continues at constant temperature, represented by the horizontal, *BC*. At *C*, solidification is complete and cooling is resumed at a rate comparable to that above the freezing point. The line *CD* represents undisturbed cooling of the solid.

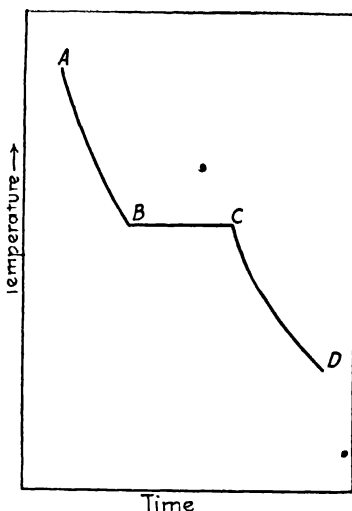


Fig. 97.—Time-temperature curve of pure metal.

The curve in Fig. 97 is idealized. Actual experimental conditions do not permit such results to be obtained. Temperature gradients in the cooling metal, and conduction of heat along the thermocouple and tube, for example, result in rounding the corners at *B* and *C*, making the exact beginning, and particularly the ending, of solidification indeterminate. There is, however, no difficulty in determining the temperature at which the bulk of the solidification takes place. The rate of cooling just below *C* is generally a little more rapid than just above *B*, because, while the metal was at the constant temperature, *BC*, its container and surroundings cooled to considerably lower temperatures, and hence increase the rate of the cooling of the metal immediately after the end of freezing. No attempt will be made here to enter

into the technique of thermal analysis. Attention is called to these points merely to emphasize the fact that the idealized curves used here for illustrative purposes are not to be expected as the result of experiment.

Molten metals often cool to a temperature below the true freezing point before solidification begins. This phenomenon is

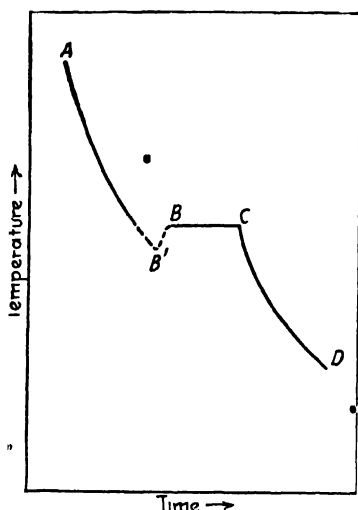


FIG. 98.—Time-temperature curve showing undercooling.

known as *undercooling*, *supercooling*, or *surfusion*. The amount of undercooling is usually a matter of only a few degrees and the latent heat of fusion is sufficient to raise the entire mass of metal to the true freezing point. This phenomenon is illustrated in Fig. 98. The horizontal, BC , represents the true freezing point of the metal. The molten metal cooled to a temperature represented by the point B' before solidification began.

In cooling and heating curves of all types the temperature of the metal under observation is usually plotted

on the vertical axis. The various types of curves differ with respect to the quantity plotted along the horizontal axis.

The *inverse-rate* curve is so named because the abscissa is the reciprocal of the rate of cooling or heating. The quantity plotted is the length of time required for the specimen to pass through successive and equal intervals of temperature. This length of time or time interval does not show any abrupt change except when there is an abnormal evolution or absorption of heat by the metal, as at the freezing point. The time interval then shows a sharp increase resulting in a cusp in the curve.

In the *direct-rate* curve the abscissa is the rate of heating or cooling, usually measured and expressed by noting the temperature change over successive and equal intervals of time. This method is little used.

The *differential* method is based on the use of a neutral body, which is placed near the test specimen so that it heats up or cools down under the same conditions. The material selected for the neutral body must be one which does not itself produce any heat effect within the temperature range under investigation, platinum, nickel, and porcelain being commonly used for the purpose. Supposing the test specimen and the neutral body to start at the same temperature, there will be little or no difference in their temperatures until some heat effect occurs in the test specimen. The heating or cooling of the test specimen will then be retarded, while that of the neutral body goes on as before. There is thereby established a temperature difference which is indicated by means of a differential thermocouple having two junctions, one in each specimen. At the same time the actual temperature of the test specimen is measured by another thermocouple. The abscissa of the differential curve is the temperature difference between test specimen and neutral body, or some quantity proportional thereto, such as the millivoltage developed by the differential couple.

The *derived-differential* curve is based on the same data as the differential but the quantity plotted as abscissa is the change in temperature difference for a constant interval in temperature. Representing the temperature of the test specimen by the letter t , and the temperature of the neutral body by t' , this quantity is given by the expression

$$\frac{(t - t')}{t}.$$

This method of plotting brings out the heat effects more sharply.

Allotropy of Iron.—There is one allotropic change in iron whose existence and importance are unquestioned. Pure iron exhibits a marked heat effect and discontinuities in most of its physical properties on being heated or cooled through a temperature of about 903° C. These changes are now known to correspond to a change in space lattice or atomic arrangement. Gamma iron, the modification stable above 903° C., has a face-centered cubic lattice, while Alpha iron, the modification stable below 903° C., has a body-centered cubic lattice.

Most of the great volume of discussion which has taken place on the allotropy of iron has centered about a small thermal arrest which reaches a maximum intensity at 768° C. The existence of this arrest in very pure iron has now been established without

question, as well as the existence of slight discontinuities in density and electrical properties. The most marked discontinuity is in magnetic susceptibility, which decreases very rapidly in the neighborhood of this temperature. It is commonly stated, and is true, in a qualitative way, that iron is magnetic below this temperature and non-magnetic above it. On the basis of such evidence it has been considered by some that there is a distinct allotropic modification of iron, called Beta iron, which is stable in the temperature range from 768 to 903° C.

Recent studies by Westgren¹ with the x-ray spectrometer have shown that in this temperature range the atomic arrangement in iron is the same body-centered cubic arrangement characteristic of Alpha iron at room temperature. The discontinuities at 768° C. are not, therefore, due to a phase change.

It is chiefly a matter of the definition of the term "allotropy" whether the change in iron at 768° C. should be called an allotropic change and Beta iron recognized as a distinct allotrope. It has been mentioned above that in this book an allotropic change is understood to involve a change in atomic arrangement. Accordingly, it will be considered that the changes at 768° C. are not due to allotropy. It may be mentioned at this point that the discontinuity at 768° C. will be omitted from the iron-carbon diagram, which is intended to show phase changes only.

More recently another allotropic transformation has been reported,² at 1,400° C., the modification stable above this temperature being called Delta iron. The existence of the transformation has been confirmed at the National Physical Laboratory in England. Westgren has reported that the x-ray spectrometer shows a body-centered cubic lattice for Delta iron, like that of Alpha iron. Further study of this change is needed. At the present time Delta iron appears to have a real existence but, because of the incompleteness of our information, it has been omitted from the diagrams of the iron-carbon system subsequently given. The Delta-Gamma transformation has not yet been shown to have any effects of practical importance in iron-carbon alloys.

The various arrests which occur in the heating and cooling of iron and steel have received designations that are universally

¹ "Roentgen Spectrographic Investigations of Iron and Steel," *J. Iron Steel Inst.*, vol. 103, p. 303, 1921.

² RUER and KLESFER, *Ferrum*, vol. 11, p. 258, 1914.

used. All the arrests are designated by the letter "A," for the French, *arrêt*. The transformations take place at different temperatures on heating and on cooling, because of lag. The letter "c," standing for *chauffage* (heating), is written after the "A" to indicate an arrest obtained on heating, while "r," standing for *refroidissement* (cooling), indicates an arrest on cooling. When the letter "A" is used alone, it is understood to refer to conditions of equilibrium, although Howe has used the letter "e" after the "A" to emphasize this distinction. For a given transformation, "Ae" lies between "Ac" and "Ar." The various critical points are distinguished from each other by numbers, written after the letters, or as subscripts.

725° C.....	A ₁	(The eutectoid change in iron-carbon alloys. Not found in pure iron.)
768° C.....	A ₂	
903° C.....	A ₃	
1,400° C.....	A ₄	

In Fig. 99 are reproduced actual heating and cooling curves of pure iron, taken by the inverse-rate method. The upper arrest, called A₃, is due to the Gamma-Alpha transformation. The beginning of the transformation is indicated by the first deviation from the substantially uniform time interval. It will be noted that the beginning of the transformation occurs at different temperatures on heating and cooling. As mentioned above, the lag in transformations in the solid state is much greater than on solidification of the liquid and, whereas it is not possible to heat a solid metal beyond its true melting point without fusion, it is the regular occurrence for a change in the solid state on rising temperature, like the Alpha-Gamma transformation, to begin at a temperature considerably above the true temperature of equilibrium between the two phases. The amount of lag increases with the rate of temperature change.

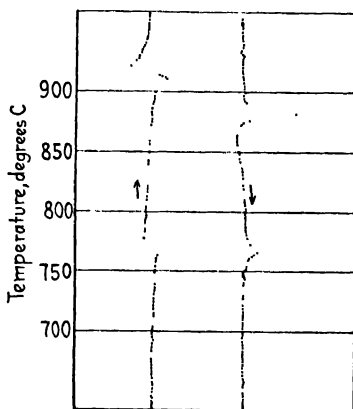


FIG. 99.—Heating and cooling curves of pure iron. (Burgess and Crowe.)

By decreasing the rate of heating and cooling, and finally extrapolating to zero rate of temperature change, Burgess and Crowe¹ found that for this zero rate the A_3 transformation begins at the same temperature on heating and on cooling, 903°C. , which is, therefore, taken as the true temperature of equilibrium between Gamma and Alpha iron.

It is also to be noted that the A_3 transformation takes place over a range of temperature, rather than at constant temperature, as in the case of the solid-liquid phase change. This is due to a number of factors, including the rigidity of the solid state, the small amount of heat evolved or absorbed, and the comparatively weak impetus to change. The tendency to change increases enormously, however, as the temperature departs from the equilibrium temperature. Thus, although the Gamma-Alpha change represented by the cooling curve occupied a good many seconds, it is impossible to prevent this change from taking place in pure iron, by quenching from above A_3 , so that the metal is down to room temperature in less than 1 sec. This means that at some temperature below A_3 the tendency of Gamma iron to change to Alpha iron is so great that the transformation is completed in less than 1 sec.

Recent ideas of atomic structure offer the basis of a plausible conception of the allotropy of iron. Many of the chemical elements exhibit two or more distinct valencies or capacities for combination, iron having a valency of either 2 or 3. It is supposed that the different valencies of an element are due to a different grouping of those outer electrons of the atom which determine the chemical properties of the element. It can be shown mathematically² that in some of the elements the electrons may be grouped in a number of different ways which are of almost equal stability.

The property of magnetism appears to depend both on atomic arrangement and on the structure of the atom itself. The iron atom seems to carry with it the possibility of magnetization, as shown by the formation of magnetic compounds, like magnetite and cementite. Yet not all aggregations of iron atoms are magnetic, as pure iron is practically non-magnetic above A_2 , and alloys of iron which permit of the retention of austenitic

¹ BURGESS and CROWE, "The Critical Ranges A_2 and A_3 of Pure Iron," *Trans. Am. Inst. Mining Eng.*, vol. 47, p. 665.

² Sir J. J. Thompson's Lectures, Franklin Institute, Apr., 1923.

(Gamma iron) solid solutions at room temperature are non-magnetic at room temperature.

Since there is no change in atomic arrangement at A_2 , the indication is that the loss of magnetism on heating above that temperature is due to a change within the iron atom. This change is considered to consist in a change in the grouping of the electrons outside of the nucleus.

This change within the atom is held to be responsible also for the allotropic or space-lattice change at A_3 . For convenience the two kinds of atom may be designated as the magnetic atom and non-magnetic atom. Molten iron solidifies on cooling in the form of Delta iron, an aggregation of non-magnetic atoms with a body-centered cubic arrangement. On further cooling to A_4 ($1,400^\circ \text{C.}$), this arrangement of the non-magnetic atoms becomes unstable and is succeeded by the face-centered cubic arrangement of Gamma iron. This grouping again becomes unstable on cooling to A_3 (903°C.) and reverts to the body-centered cubic arrangement, forming Alpha iron. It is difficult to see why this arrangement, which lost its stability at $1,400^\circ \text{C.}$, should again become stable, unless it is supposed that the new allotrope, Alpha iron, is made up, at least partly, of a different kind of atom, *i.e.*, the magnetic atom. Since the Gamma to Alpha change takes place 135°C. above A_2 , it must be supposed that the intra-atomic change which reaches its culmination at A_2 begins at a considerably higher temperature, that is, above A_3 .

The ferromagnetic elements, nickel and cobalt, undergo physical changes, including loss of magnetism, at temperatures of about 350 and $1,100^\circ \text{C.}$ respectively. It has been demonstrated in the case of nickel that this change is not accompanied by a change of space lattice. It is probable that the magnetic changes in these elements are analogous to the A_2 change in iron, and depend on changes of electron grouping in the nickel atom and the cobalt atom. Both nickel and cobalt exhibit two different chemical valencies.

Molten Alloys.—A pair of liquids may be miscible in all proportions, like water and alcohol, or may be practically immiscible, like water and oil, or may possess a partial mutual solubility, like water and phenol. Generally, the extent of such limited solubility increases with rise in temperature, and there is, theoretically, a critical temperature above which the liquids are completely miscible. This temperature may, however, lie above the

boiling point of one or both of the liquid phases and so may not be actually realizable. The solubility relations may be illustrated by the system, *water-phenol*, which is typical of some metallic systems and has probably been more thoroughly studied.

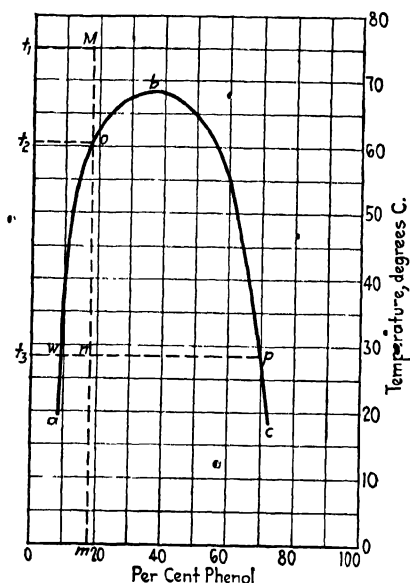


FIG. 100.—Solubility relations of water and phenol.

In the diagram, Fig. 100, the proportion of phenol in the mixture is represented on the horizontal axis, and temperature on the vertical axis. The line *abc* is the solubility curve of water and phenol under atmospheric pressure. Above this curve there is only one liquid phase, while below there are two liquid phases, one rich in water and the other rich in phenol. The critical solution temperature is represented by the point *b* (68.4° C.). Above this temperature there can be only one liquid phase, no matter what the proportions of water and phenol in the mixture.

All points on the line *Mm* represent a mixture containing *m* per cent of phenol and (100-*m*) per cent of water. At the temperature *t*₁, corresponding to the point *M*, there is one liquid phase. At *t*₃, corresponding to the point *n*, there are two liquid phases in equilibrium, the compositions of which are represented by the points *w* and *p* where the solubility curve *abc* is cut by a

horizontal through n . The temperature t_2 , corresponding to the point of intersection, o , is the temperature at which the second liquid phase forms on cooling and disappears on heating.

In most alloy systems of commercial interest the components are mutually soluble in all proportions in the liquid state, and there is only one liquid phase to consider. In fact, complete liquid miscibility is sometimes stated to be an essential characteristic of a true alloy. The word "alloy" as commonly used, however, includes some systems in which two liquid phases are formed. A familiar example is that of the copper-lead alloys. At ordinary melting temperatures, such as $1,150^\circ \text{C}$. these two metals are not completely miscible, and a mixture containing, say, 50 per cent of each separates into two liquid phases, one rich in copper and the other rich in lead. As the temperature rises, the solubility of each metal in the other (molten) metal increases, and probably at some temperature complete miscibility occurs, although it may not be possible to realize this condition under ordinary pressure because of the relatively low boiling point of lead.

Binary Alloy Systems.—The phase changes which take place in binary alloys during and after solidification are of considerable variety, and the solidification phenomena, in particular, have served as a basis for schemes of classification of the alloys. For present purposes there seems to be no advantage in following any formal classification, especially since there is no standard or generally accepted system of classification. The various types of phenomena will be illustrated by the description of certain typical alloy systems. These systems have been selected because of their commercial importance as well as their illustrative value.

The constitution of an alloy system is expressed in the diagram of thermal equilibrium. For a system consisting of two metals, this diagram is a plane figure, plotted on rectangular coordinates, the horizontal axis representing composition and the vertical axis temperature. Composition is expressed in per cent. It was formerly quite common to express composition in terms of atomic per cent, in the attempt to trace the effects of atomic proportions, but this method of plotting has been largely abandoned because of the lack of sharp atomic relations, and the practical inconvenience of figuring in atomic percentages.¹ It is occasionally desirable for special purposes to plot the composition by volume. For

¹ X-ray work may give new usefulness to atomic per cents.

general purposes, however, it is standard practice to represent composition in terms of per cent by weight. Temperature is almost invariably expressed in the Centigrade scale. The method is illustrated in Fig. 101, representing the constitution of alloys of copper and nickel.

Copper-nickel.—Copper and nickel are quite similar metals. They possess nearly equal atomic weights, practically identical

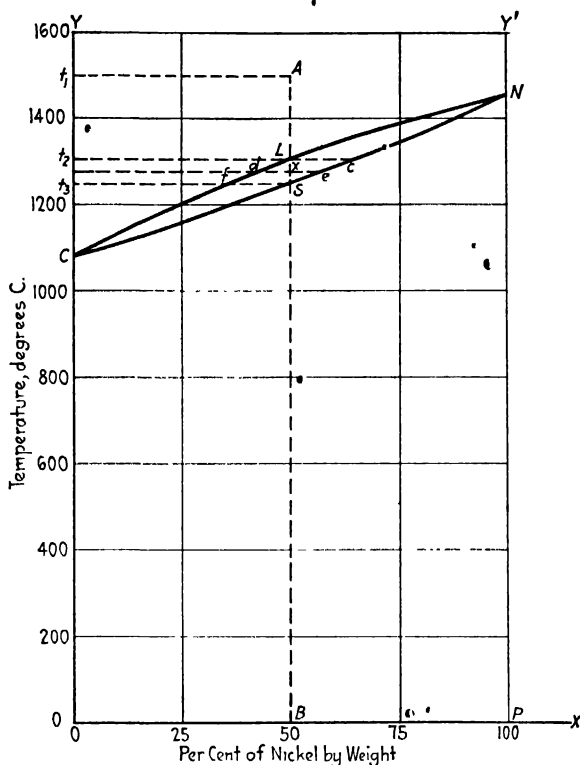


FIG. 101.—Constitution diagram of the copper-nickel alloys.

atomic volumes, and crystallize with space lattices (face-centered cubic) which are almost identical, both as to pattern and dimension. According to Langmuir's conceptions, the two elements resemble each other closely even in the structure of their atoms. It is therefore quite consistent that in the alloys of copper with nickel the atoms of one element are almost interchangeable with those of the other. There is complete solubility in both liquid

and solid states, hence only one liquid phase and one solid phase. All of the alloys solidify through a range of temperature rather than at constant temperature, and the temperatures at which solidification begins all lie between the freezing points of the two pure components, copper and nickel. There are no known phase changes in the solid state.

These facts are expressed in the constitutional diagram, Fig. 101. At the origin of the axes (point O) there is pure copper, at a temperature of 0°C . All points on the axis OY represent pure copper. The *concentration* of nickel is zero in "alloys" represented by these points. The proportion of nickel is represented along the axis OX by figures from 0 to 100. The point P represents an alloy containing 100 per cent nickel, that is, pure nickel. All points on the vertical line PY' represent pure nickel. Points between O and P on the horizontal axis represent alloys containing the expressed percentage of nickel and a percentage of copper equal to $100 - \text{Ni}$, where Ni is the per cent nickel. The per cent copper may be shown on a second horizontal scale if desired. There is no established convention as to which side of the diagram should be chosen to represent any particular metal, except that when only a portion of the diagram is shown it is usual to represent the pure metal at the left. There is likewise no established convention regarding the range of temperature covered by the temperature scale. It is perhaps most common to begin the diagram at room temperature, and extend it upward beyond the highest melting point involved. Frequently, however, the constitution of the alloys in the solid state is not shown, so the temperature scale may begin above room temperature.

The line CLN on the diagram shows the temperatures at which copper-nickel alloys of various compositions begin to freeze on cooling or become completely molten on heating. This line is called the *liquidus*. The line CSN , called the *solidus*, represents the temperatures at which solidification is complete on cooling or at which fusion begins on heating. To take a specific example, consider an alloy containing equal parts of copper and nickel, at such a temperature (t_1) that it is completely molten. The condition of the alloy is represented by the point A , which defines its composition and temperature. Now suppose the alloy is allowed to cool, the cooling being represented by the line AB . At the point L the line AB intersects the liquidus CLN . This indicates the temperature (t_2) at which solidification begins. The

material that begins to freeze out of the liquid is a solid solution of copper and nickel, richer in nickel than the alloy as a whole. The molten metal is thereby made richer in copper, and further freezing takes place only as the temperature is lowered. Solidification is complete at a temperature, t_3 , corresponding to the intersection, S , of the line AB with the solidus CSN . Cooling continues along SB without further change of state. Points above the liquidus CLN represent alloys in a completely molten condition. Within the area $CLNS$ the alloys are partly solid and partly liquid, and below the line CSN , they are completely solid.

The diagram not only gives these qualitative facts, but also furnishes quantitative information as to the compositions and relative proportions of the solid and liquid phases in equilibrium with each other within the area $CLNS$. Thus, the composition of the solid solution, which under equilibrium conditions begins to freeze out of the liquid at the point L , is represented by the point c , at the intersection of the solidus CSN with a horizontal through the point L . At any point, x , within the two-phase region, the compositions of the solid and liquid phases in equilibrium with each other are given by the intersections of a horizontal through x , with the solidus and liquidus curves respectively. That is, at the point x in the diagram, the composition of the liquid phase is represented by the point d , while the composition of the solid phase is represented by the point e . The relative proportions of the two phases are given by the so-called "lever principle," which may be expressed as follows:

$$\frac{\text{Amount of solid}}{\text{Amount of liquid}} = \frac{dx}{xe}$$

These rules are of general application in two-phase fields.

The composition of the liquid phase remaining at the end of solidification at the point S is represented by the point f , where a horizontal intersects the liquidus. This point also, of course, represents the composition of the first liquid to form on heating the solid alloy.

There are several compositions of copper-nickel alloys now in common commercial use. The most prominent ones are the following:

1. Two and one-half per cent (2.5 per cent of nickel) cupro-nickel for driving bands of shells.
2. Fifteen per cent cupro-nickel, used largely for bullet jackets and by the United States Navy for condenser tubes and feed water heaters, containing from 14 to 16 per cent of nickel.

3. Nickel-bronze, or coinage bronze, used for baser currency and containing 25 per cent of nickel.

4. Copper nickel, containing 50 per cent of nickel, used for remelting in the manufacture of nickel-copper alloys.

5. Constantan, used as one element in the construction of thermocouple pyrometers and also as electrical-resistance wire, containing 45 per cent of nickel.¹

Monel metal is an alloy of somewhat variable composition, but containing approximately 67 per cent nickel, 28 per cent copper, and smaller amounts of other metals, chiefly iron and manganese. It is characterized by high tensile strength, ductility, and resistance to corrosion. A recent development is the addition of a small amount of aluminum, about 3 per cent, which increases the strength and particularly the elastic limit.

The nickel silvers are alloys of copper, zinc, and nickel in varying proportions, the nickel being used to whiten the alloy. The amount of nickel is perhaps most commonly about 20 per cent. All the alloys mentioned above are of the solid solution type and consist structurally, after mechanical working and annealing, of a single homogeneous solid solution based on the copper or the practically identical nickel space lattice.

Copper-gold.—In the copper-nickel system the melting points of all the alloys lie between those of the two components. This is not necessarily the case in a solid solution series. Theoretically, the freezing point curve may exhibit either a maximum or minimum. No alloy system of the solid solution type is known in which the freezing point curve passes through a maximum, but a minimum is sometimes found.

Such a system is formed by copper and gold, as shown in the equilibrium diagram of Fig. 102. The freezing point curve passes through a minimum at the point A. It will be noted that at this composition the liquidus and solidus curves touch. In other words, the alloy solidifies at constant temperature. On either side of this point the solidification phenomena are similar to those of the copper-nickel system.

Copper and gold both crystallize with the face-centered cubic arrangement of atoms, and form a continuous series of solid solutions.

Copper is the most common hardener and adulterant of gold, and the alloys are extensively used for coinage and jewelry.

¹ "Nickel," *Cir.* 100, Bureau of Standards.

The standard gold coinage of the United States contains 10 per cent copper. The amount of copper used in "gold" for ornamental purposes may exceed 50 per cent.

Lead-antimony.—Lead and antimony form neither solid solutions nor chemical compounds, but they are completely miscible in the liquid state. The melting point of each element

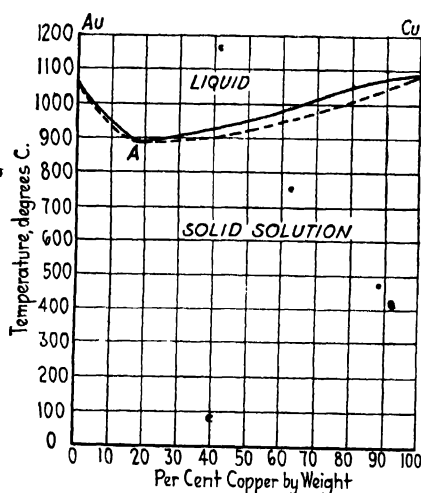


FIG. 102.—Constitution diagram of the copper-gold alloys.

is lowered by the addition of the other until a minimum is reached for a mixture containing 13 per cent of antimony. The phenomena of solidification can best be described by reference to the equilibrium diagram of Fig. 103.

The upper curve, *LEA*, is the liquidus, above which the alloys are completely molten.

The horizontal, *TEC*, is the solidus, below which the alloys are completely solid. The areas *TEL* and *CEA* represent conditions of composition and temperature under which the alloys are partly solid and partly liquid. There are no phase changes in the solid state.

Consider an alloy represented by the point *X*, containing more than 13 per cent antimony. On cooling the melt, solidification begins at the temperature t_1 , corresponding to the point *o*, where the vertical *Xx* intersects the liquidus branch, *EA*. The solid phase which separates from the melt is nearly pure

antimony, and by its separation the melt is enriched in lead. This lowers the freezing point and further solidification takes place only on falling temperature, additional antimony freezing out and thereby progressively enriching the liquid phase in lead.

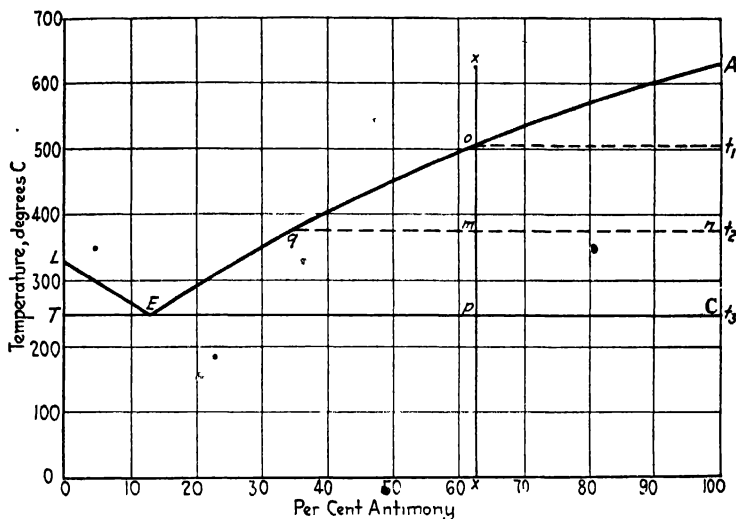


FIG. 103.—Constitution diagram of the lead-antimony alloys.

At any given temperature the compositions and relative proportions of the solid and liquid phases can be determined by the methods described above for the copper-nickel system. At the temperature t_2 , for example, the composition of the liquid phase is represented by the point q , where a horizontal intersects the liquidus. The composition of the solid phase, *i.e.*, antimony, is represented by the point n , where the horizontal intersects the other boundary of the two-phase field, AC . The relative amounts of solid and liquid are given by the proportion—Amount of solid: amount of liquid :: qn : mn .

This freezing process continues until the temperature of the solidus, t_3 , is reached. At this point the composition of the liquid phase is represented by the point E . This remaining liquid now solidifies at constant temperature forming an intimate mixture of lead and antimony crystals. The term *eutectic*, meaning “lowest melting,” is applied to the alloy composition, to the solid mixture, and to the temperature of solidification. The significance of the eutectic will be understood somewhat better after considering alloys near the lead end of the series.

Alloys containing less than 13 per cent antimony solidify in a manner entirely analogous to that just described, except that the solid phase which first separates from the liquid is lead instead of antimony. The melt is thereby enriched in antimony and its composition again approaches the point *E*, reaching that value when the temperature has fallen to t_3 . The liquid remaining at this point then solidifies at constant temperature, forming the eutectic mixture of lead and antimony.

It is thus seen that, no matter what the composition of the alloy started with, solidification always ends at the same temperature with the freezing of a portion of the liquid which has reached eutectic composition. The branch *LE* of the liquidus may be regarded as the solubility curve of lead in lead-antimony liquid solutions; while the branch *AE* is the solubility curve of antimony in such solutions. At the point *E* the solution is saturated with respect to both lead and antimony, and lowering of the temperature results in the simultaneous precipitation of both metals. Obviously, if one starts with a molten alloy having exactly the composition of the eutectic, no solid will freeze out until the eutectic temperature is reached, when the whole alloy will solidify at constant temperature.

Various terms are applied to the constituents which freeze out before the eutectic, the most common being *primary*, *excess*, and *pro-eutectic*. For example, in a solid alloy containing more than 13 per cent antimony, the antimony present is of two kinds or forms, which may be described as primary or excess antimony and eutectic antimony.

The amounts of eutectic and of excess constituent which will form on the solidification of any alloy may be readily calculated. When the alloy contains 13 per cent antimony, it consists entirely (100 per cent) of eutectic, while with no antimony present the percentage of eutectic is zero. Between these extremes the percentage of eutectic present is a linear function of the percentage of antimony. For example, an alloy containing 4 per cent antimony consists of $\frac{4}{13} \times 100 = 30.8$ per cent eutectic and 69.2 per cent excess lead. For alloys on the other side of the eutectic the computation may conveniently be made in terms of lead. Thus an alloy containing 40 per cent antimony contains 60 per cent lead. The eutectic contains 87 per cent lead. The alloy therefore contains $\frac{20}{17} \times 100 = 69$ per cent eutectic and 31 per cent excess antimony.

Lead-antimony alloys containing up to 20 per cent antimony are used for bearings, type metal, shot, battery plates and grids.

Silver-copper.—Theoretically, it is probable that no two metals are completely insoluble in each other. For purposes of illustration, however, lead and antimony may be considered insoluble in each other in the solid state, just as oil and water are in the

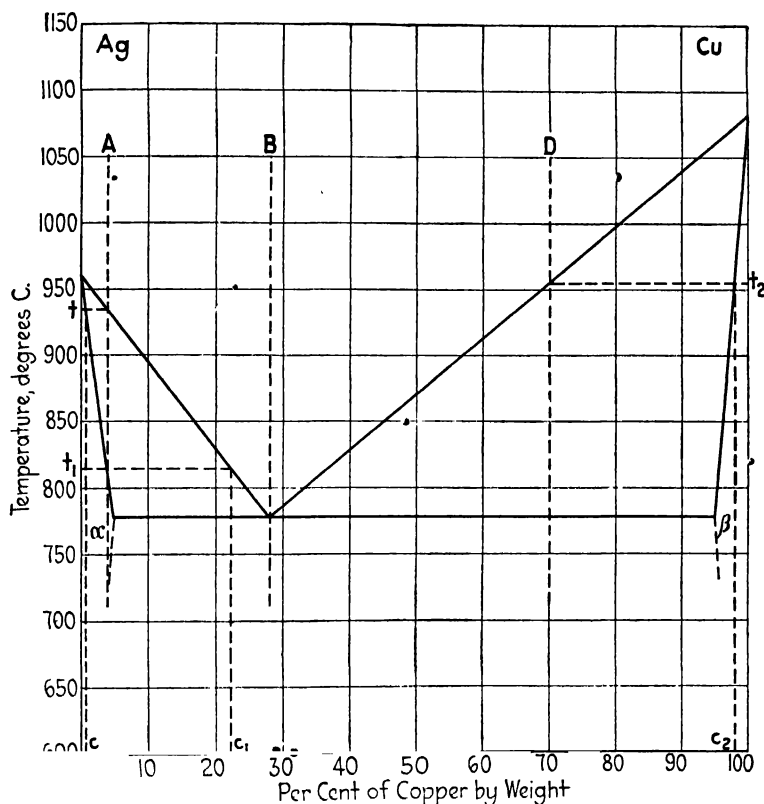


FIG. 104 — Constitution diagram of the silver-copper alloys.

liquid state. There are several eutectiferous systems in which quite appreciable solid solubility does occur. Silver, melting at 961° C., and copper, melting at 1,083° C., form a eutectic containing 28 per cent copper and melting at 778° C. Copper dissolves in solid silver at the eutectic temperature to the extent of about 5 per cent, and solid copper will hold in solution about 5 per cent of silver.

The equilibrium diagram of this system is shown in Fig. 104.

The equilibria of three alloys will be considered, namely, alloys *A*, *B*, and *D*, containing 4.0, 28 and 70 per cent copper respectively.

Liquid alloy *A*, when cooled, begins to freeze at temperature *t*. The first metal to freeze has a composition represented by *c*. At any temperature between *t* and *t*₁ the alloy is partly liquid and partly solid. The intersection of a horizontal line, representing any given temperature between *t* and *t*₁, with the solidus line gives the average composition of the solid metal for that temperature, and the intersection of the same horizontal line with the liquidus line represents the composition of the remaining liquid. At temperature *t*₁, the alloy becomes completely solid, the last liquid to solidify having a composition *c*₁. Under practical casting conditions, the solid alloy may contain some segregation of a copper-rich constituent (Beta) because of the high copper content of the last liquid to solidify. This would then be a "cored" structure. If sufficient time be allowed in cooling from *t*₁ to produce equilibrium conditions, the composition will be equalized by diffusion and the solid alloy will consist entirely of unsaturated Alpha solid solution. All alloys containing less than 5 per cent copper would be referred to as unsaturated Alpha solutions, and the 5 per cent alloy would be referred to as saturated Alpha solid solution.

B is the eutectic alloy and consists structurally of saturated Alpha and saturated Beta solid solutions. Saturated Alpha and Beta solid solutions may be regarded as the two components of a binary system of the simple eutectiferous type. To calculate the percentages of each constituent in the eutectic alloy the lever principle is again applied.

In calculating amounts of constituents in eutectics, or the amount of eutectic or excess substance in binary systems, this principle may be applied as follows: To determine the per cent of any constituent in a given alloy, first find the number of units on the composition scale within which the constituent varies from zero to 100 per cent. Call this value *M*. Next find the number of units on the composition scale between the points of zero per cent of the desired constituent and of the alloy in question. Call this value *N*.

Then

$$\frac{N}{M} \times 100 = \text{the per cent of the constituent in the alloy.}$$

For example, to find the per cent of Alpha in the eutectic alloy, it is first noted that at 5 per cent copper there is 100 per cent saturated Alpha, and that at 95 per cent copper there is zero per cent Alpha. The number of units on the composition scale between zero and 100 per cent saturated Alpha is $95 - 5 = 90$, or M . Alloy B contains 28 per cent copper. The number of units on the composition scale between this alloy and the point of zero Alpha is $95 - 28 = 67$, or N .

$$\frac{67}{90} \times 100 = 74.44 \text{ per cent Alpha in the eutectic alloy.}$$

The amount of Beta is $100 - 74.44 = 25.56$ per cent. This alloy freezes at constant temperature, 778°C .

Alloy D , containing 70 per cent copper, on cooling from above the liquidus begins freezing at temperature t_2 , unsaturated Beta of composition c_2 being the first material to freeze out. At all temperatures between t_2 and the freezing point of the eutectic the alloy is partly liquid and partly solid. At any temperature between t_2 and the freezing point of the eutectic the average composition of the solid portion is represented by the intersection of the horizontal temperature line with the solidus line, and the composition of the liquid portion is represented by the intersection of the same temperature horizontal line with the liquidus line. All of the solid freezing out before the liquid has reached eutectic composition is excess Beta. When the liquid portion reaches eutectic composition it freezes on further cooling, as eutectic. The solid alloy, assuming equilibrium, consists of excess saturated Beta and eutectic. To find the amounts of each, the per cent eutectic can be calculated. At 28 per cent copper there is 100 per cent, and at 95 per cent copper there is zero per cent eutectic; $95 - 28 = 67$ units = M ; 95 (point of zero per cent eutectic) $- 70$ (copper in alloy) $= 25 = N$.

$$\frac{25}{67} \times 100 = 37.31 \text{ per cent eutectic.}$$

$$100 - 37.31 = 62.69 \text{ per cent excess saturated Beta.}$$

Calculating for total Alpha and Beta in alloy D , $M = 90$. N , for Alpha $= 95 - 70 = 25$.

$$\frac{25}{90} \times 100 = 27.78 \text{ per cent total Alpha.}$$

$$100 - 27.78 = 72.22 \text{ per cent total Beta.}$$

All of the Alpha is in the eutectic. Since the total amount of the eutectic is 37.31 per cent and the total amount of Alpha is 27.78 per cent and all the Alpha is in the eutectic, the Beta in the eutectic is $37.31 - 27.78 = 9.53$ per cent.

The excess Beta plus the Beta of the eutectic equals the total Beta obtained by the independent calculation.

$$9.53 + 62.69 = 72.22 \text{ per cent total Beta.}$$

Between 5 per cent and 28 per cent copper the alloys would consist of excess saturated Alpha and eutectic. The calculation for the per cent eutectic in this range would be made on the basis of zero eutectic at 5 per cent copper and 100 per cent eutectic at 28 per cent copper.

Sterling silver and other silver coinage alloys are silver-copper alloys. Sterling silver containing 92.5 per cent silver is extensively used for high grade tableware and has been used for coinage in Great Britain and some of the British Colonies. In the United States the coinage alloy contains 90 per cent silver and 10 per cent copper.

Magnesium-silicon.—Magnesium and silicon form a definite compound containing 37 per cent silicon, represented by the formula Mg_2Si . A eutectic occurs at 4 per cent silicon, the constituents of which are magnesium and the compound, magnesium silicide. Another eutectic consisting of magnesium silicide and silicon is formed at 58 per cent silicon. So far as is known, the compound is not appreciably soluble in either magnesium or silicon in the solid state.

The equilibrium diagram, shown in Fig. 105, is most easily understood by dividing it into two portions, at the composition of the compound. Alloys containing up to 37 per cent silicon may be regarded as constituting a binary system, of which the components are magnesium and magnesium silicide. This is then a simple eutectiferous system entirely analogous to the lead-antimony system. The alloys containing 37 to 100 per cent silicon constitute a second similar binary system whose components are magnesium silicide and silicon.

An alloy of the exact composition required to form the compound, Mg_2Si , solidifies at constant temperature. The two eutectics also solidify entirely at constant temperature but, it will be noted, not at the same temperature. All other alloys of the system freeze over a range of temperature, exactly as in

the lead-antimony system. A cooling curve of the alloy represented by the point *A*, for example, would show two arrests, one at t_1 , corresponding to the freezing out of primary silicon, and the other at t_2 , corresponding to the solidification of the

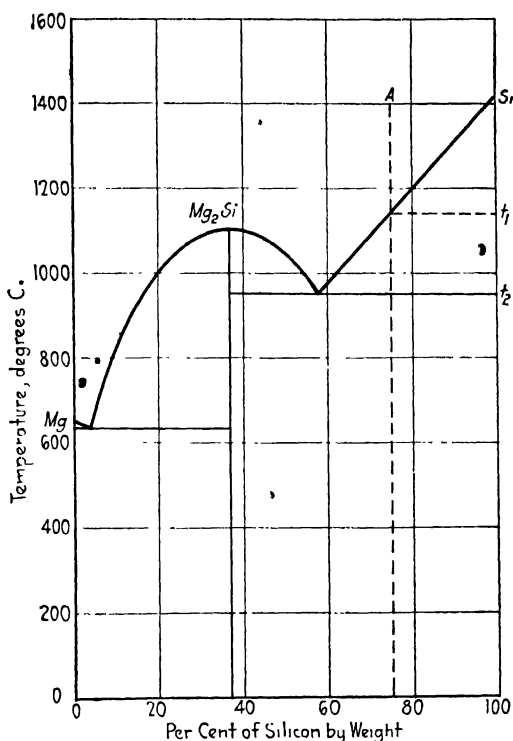


FIG. 105.—Constitution diagram of the magnesium-silicon alloys.

magnesium silicide-silicon eutectic. The constitution of the solid alloys is summarized in the following tabulation:

COMPOSITION, PER CENT SILICON	CONSTITUENTS OF SOLID ALLOY
0 to 4	Primary Mg + eutectic of Mg and Mg_2Si .
4 to 37	Primary Mg_2Si + eutectic of Mg and Mg_2Si .
37	Mg_2Si .
37 to 58	Primary Mg_2Si + eutectic of Mg_2Si and Si.
58 to 100	Primary Si + eutectic of Mg_2Si and Si.

General Attributes of Binary Eutectics.—The occurrence of binary eutectics of various types has now been illustrated and a brief summary may be given of their general attributes:

1. The eutectic contains its components in definite proportions, but usually not in simple atomic or formula weight proportions.

2. The solid eutectic alloy is an intimate physical mixture of two phases, which may be (a) pure metals or metalloids, (b) solid solutions, or (c) compounds.

3. The eutectic alloy has the lowest melting point of any of the alloys made up of the same two phases.

4. The eutectic alloy melts and freezes at constant temperature.

Aluminum-copper.—Aluminum and copper combine in definite proportions to form the compound, CuAl_2 , containing 54 per cent copper. The present discussion will be confined to alloys containing less than this amount of copper. Copper is soluble in solid aluminum up to about 5 per cent. A eutectic is formed containing 33 per cent of copper and freezing at 542°C . The constituents of this eutectic are the compound, CuAl_2 , and the solid solution of copper in aluminum. The solubility of copper in solid aluminum reaches the maximum value of approximately 5 per cent at the eutectic temperature, and decreases progressively as the temperature is lowered until at room temperature it is less than 3 per cent.

These facts are represented in the equilibrium diagram, Fig. 106, in which AEC is the liquidus, ABK the solidus, and SB the solubility curve of copper in solid aluminum. The line BK is the eutectic horizontal, the eutectic being represented by the point E . The point C represents the compound, CuAl_2 , at its melting point.

The solid phase which separates from liquid alloys containing 33 to 54 per cent copper as they cool to the line EC is the compound, CuAl_2 . This constituent continues to freeze out until the eutectic temperature is reached, when the remainder of the liquid is of eutectic composition and solidifies at constant temperature as a mixture of the compound, CuAl_2 , and the aluminum-rich solid solution whose copper content is represented by the point B . On cooling to room temperature, this solid solution precipitates CuAl_2 in accordance with the solubility curve, SB .

The solid phase which first separates from liquid alloys containing up to 33 per cent copper is the aluminum-rich solid solution. In alloys containing more copper than that represented by the point B , solidification again ends with the freezing of the eutectic at BK .

The phase changes taking place on cooling from the molten state will be considered in detail for the alloy represented by the point X . At the temperature t_1 , corresponding to the intersection of the vertical Xx with the liquidus AE , solidification begins with the separation of a solid solution of copper and aluminum. The composition of this solid solution is represented by the point p , where a horizontal through m intersects the solidus AB . As cooling continues, both the liquid and solid phases

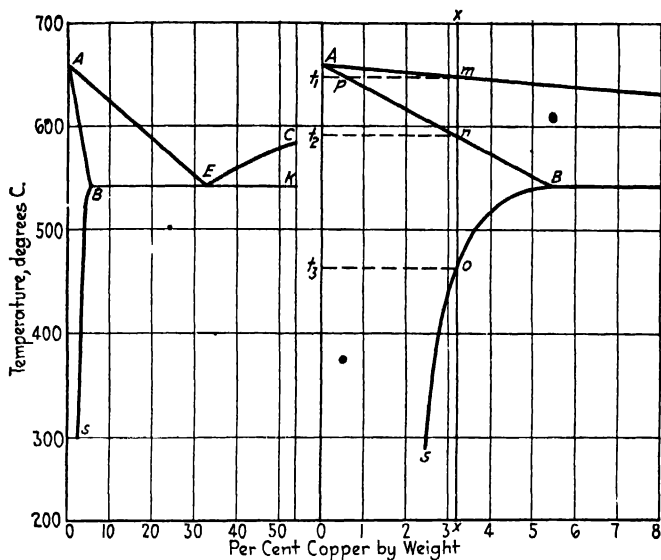


FIG. 106.—Constitution diagram of the aluminum-copper alloys.

become richer in copper, their compositions following the lines AE and AB respectively. At the temperature t_2 , corresponding to the point of intersection, n , of the vertical Xx with AB , solidification is complete. At t_3 the solid solution is saturated with copper, and the compound, CuAl_2 , begins to form. On further cooling this phase continues to separate in accordance with the solubility curve, SB .

The phases present in the various fields of the equilibrium diagram are as follows:

Above AEC , one liquid phase.

Area AEB , solid solution + liquid.

Area CEK , CuAl_2 + liquid.

Area ABS , solid solution.

Under SBK , solid solution + CuAl_2 .

Aluminum-magnesium silicide.—It has been mentioned above that alloys of aluminum, magnesium, and silicon may be regarded as constituting a binary system, provided the magnesium and silicon are present in the proportions required to form the compound, Mg_2Si . The two components are then aluminum and magnesium silicide. It will at once be seen from the equilibrium diagram, Fig. 107, that the system is similar to that formed by aluminum and $CuAl_2$, just described. Aluminum-rich solid solutions are formed containing magnesium and silicon in the proportions required to form the compound. The solubility of

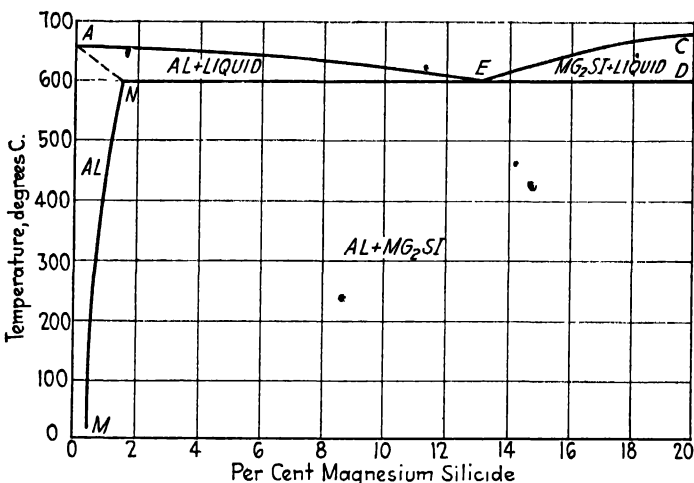


FIG. 107.—Constitution diagram of the alloys of aluminum with magnesium silicide.

the compound in aluminum decreases with the temperature, just as in the case of $CuAl_2$. The eutectic mixture consists of the compound, Mg_2Si , and the solid solution.

Iron-cementite.—Iron and carbon form a hard, crystalline compound, known metallographically as cementite, whose composition is represented by the formula Fe_3C . The theoretical carbon content of this compound is 6.67 per cent. Interest in the iron-carbon system is confined to alloys containing less than this amount of carbon.

The equilibrium diagram is given in Fig. 108. If, for the moment, only the part of the diagram above $900^\circ C$ is considered, it is apparent that the system closely resembles the $Al-CuAl_2$ system. Carbon dissolves in Gamma iron up to a maximum of

about 1.7 per cent, at the eutectic temperature. The various constituents of the iron-carbon alloys, both simple and complex, have been given specific names which are quite generally recognized. The Gamma iron solid solutions are designated by the term *austenite*, after Roberts-Austen. The eutectic at 4.3 per cent carbon consists of austenite and cementite. The proportions of cementite and austenite in the eutectic, at the eutectic temperature, may be calculated by the lever principle discussed above.

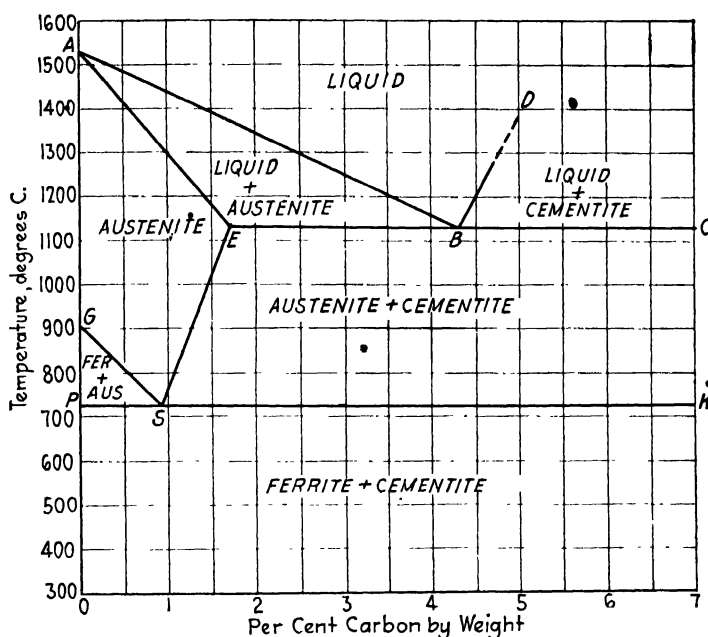


FIG. 108.—Constitution diagram of iron-cementite system.

At 1.7 per cent carbon there is zero cementite, and at 6.67 per cent carbon there is 100 per cent cementite. The base line is $6.67 - 1.7 = 4.97$ units. The eutectic alloy is $4.3 - 1.7 = 2.6$ units from the point of zero cementite.

$$\frac{2.6}{4.97} \times 100 = 52 \text{ per cent cementite in eutectic alloy.}$$

$$100 - 52 = 48 \text{ per cent austenite in eutectic alloy.}$$

The line *SE* is the solubility curve of cementite in austenite, and it will be noted that the solubility decreases with falling temperature.

The allotropic transformation (Gamma to Alpha) in iron gives rise to very important phase changes in the solid state, resulting from an abrupt decrease in solvent power for carbon. Saturated austenite at 900° C. contains about 1.2 per cent carbon, whereas it is probable that Alpha iron does not dissolve much over 0.05 per cent carbon. It is almost universal practice, in the construction of the equilibrium diagram, to represent complete insolubility of carbon in Alpha iron, and it is quite common to say that carbon is "insoluble" in Alpha iron in discussing the system. This is not correct, inasmuch as the solubility, slight though it is, is sufficient to enable important structural changes to take place by the process of diffusion, as will be described in a later chapter. However, the solubility is represented as zero in the diagram of Fig. 108 (in accordance with the general practice), because the actual values are not known.

The temperature of transformation of Gamma iron to Alpha iron is lowered by the presence of carbon in solid solution. The line *GS* gives the temperature at which Alpha iron (ferrite) forms from austenite containing various amounts of carbon. This line may be regarded as the solubility curve of ferrite in austenite. At the point *S*, where the solubility curve of ferrite intersects the solubility curve of cementite, the solid solution (austenite) is saturated with respect to both ferrite and cementite, and both of these phases are precipitated at constant temperature and with a considerable evolution of heat, as an intimate mixture which, from its analogy to a eutectic, is termed the *eutectoid*. With ordinary rates of cooling, the eutectoid is made up of alternate thin lamellae of ferrite and cementite, and under the microscope acts as a diffraction grating giving rise to a play of colors suggestive of mother-of-pearl. The name *pearlite* is applied to the constituent and also to the phase change, as in the expressions "pearlite transformation" and "pearlite arrest."

From the viewpoint of the phase doctrine, the changes taking place below 900° C. in the iron-cementite system are strictly analogous to those taking place on the solidification of a simple eutectiferous system, like the lead-antimony system. The homogeneous solid solution, austenite, corresponds to the liquid lead-antimony alloys. When an iron-carbon alloy containing less than the eutectoid ratio of carbon cools to the temperature given by the line *GS*, ferrite separates from the solid solution, just as lead separates from molten lead-antimony alloys contain-

ing less than 13 per cent antimony on reaching the liquidus. As the temperature falls, the remaining austenite is progressively enriched in carbon, just as the liquid lead-antimony solution is enriched in antimony, and finally reaches the composition of the eutectoid. The residual austenite of eutectoid composition then decomposes at constant temperature to form pearlite. Starting with an alloy containing more than 0.90 per cent carbon, a similar process takes place, except that the excess phase is cementite instead of ferrite.

Steels containing less than the eutectoid percentage (0.90) of carbon are designated *hypo-eutectoid*, while alloys containing more than this amount of carbon are called *hyper-eutectoid*. Alloys containing less than the eutectic percentage (4.3) of carbon are correspondingly termed *hypo-eutectic*, and those containing more than the eutectic ratio *hyper-eutectic*. The austenite that freezes out of the hypo-eutectic alloys above the eutectic temperature is usually distinguished as *primary austenite*, while the austenite of the austenite-cementite eutectic (Ledeburite) is called *eutectic austenite*. Similarly, the cementite that freezes out of the hyper-eutectic alloys above the eutectic temperature is referred to as *primary cementite*, and that of the eutectic itself as *eutectic cementite*. The ferrite that forms from hypo-eutectoid austenite on cooling through the thermal critical range (900 to 725° C.) is called *pro-eutectoid ferrite*, and the cementite precipitated from hyper-eutectoid alloys on cooling to 725° C. is called *pro-eutectoid cementite*. The ferrite and cementite of the eutectoid itself are designated by the prefix "eutectoid," or sometimes "pearlitic."

Although there are only two phases, ferrite and cementite, present in the alloys at room temperature, there may be two forms of ferrite or as many as four forms of cementite, distinguished by their origin. Thus in hyper-eutectic cast iron there may be primary cementite, eutectic cementite, pro-eutectoid cementite (formed from the eutectic austenite on cooling from 1130 to 725° C.), and eutectoid cementite.

The phase changes taking place on cooling will be considered in detail for a number of iron-carbon alloys selected to represent the various types encountered in the system. The molten alloys are represented in the diagram, Fig. 109, by points *M*, *N*, *O*, *P*, and *R* above the liquidus. Vertical lines dropped from these points represent the condition of the alloys on cooling, phase

changes taking place when the verticals intersect the lines of the equilibrium diagram.

Alloy *M*, carbon 0.35 per cent, is typical of the hypo-eutectoid steels, and is widely used for forgings requiring combined strength and toughness. Solidification begins at the point 1 with the separation of primary austenite of the composition represented by the point 2. Freezing continues on falling temperature, both the solidifying austenite and the residual liquid becoming

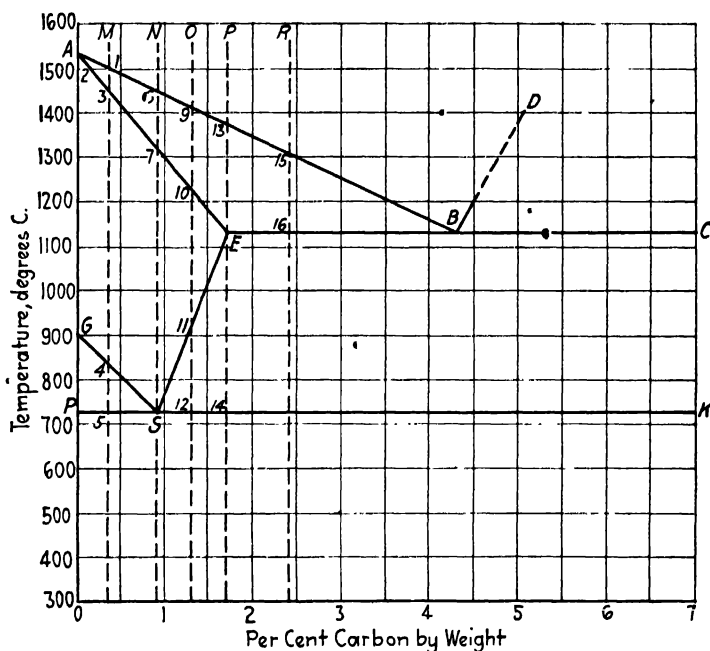


FIG. 109.—Phase changes in various alloys of the iron-cementite system.

gradually richer in carbon. It is supposed, however, that the rate of cooling is sufficiently slow that the austenite becomes homogeneous by the process of diffusion. Solidification is then complete at the point 3, and the solid alloy consists entirely of austenite of a uniform carbon content of 0.35 per cent. No further change occurs until the alloy has cooled to the point 4, where pro-eutectoid ferrite begins to precipitate. The amount of ferrite increases as the temperature falls, the residual austenite becoming correspondingly richer in carbon. At the point 5

the austenite has reached the eutectoid composition, and breaks down at constant temperature, forming the eutectoid mixture of ferrite and cementite, known as "pearlite." The alloy now consists structurally of $100 \times \frac{0.35}{90} = 39$ per cent pearlite, and 61 per cent pro-eutectoid ferrite. The pearlite itself is made up of $100 \times \frac{0.90}{6.67} = 13$ per cent cementite and 87 per cent ferrite. These calculations are based on the assumption that ferrite holds no carbon in solution, an assumption not strictly correct but sufficiently close for these calculations. No further phase changes take place during cooling from the eutectoid to the ordinary temperature, unless the possibility of a slight additional precipitation of cementite from the very dilute Alpha iron solid solution is considered. This is not indicated in the diagram. A magnetic change occurs in cementite at about 215° C., but there is probably no corresponding phase change.

Alloy *N* is of eutectoid composition. Steels of this carbon content (0.90 per cent) are used for springs and tools. Solidification begins at the point 6, with the separation of primary austenite from the liquid, and is complete at the point 7. The alloy then consists entirely of austenite, which cools without further change to the eutectoid temperature. At this point, *S*, the austenite of eutectoid composition decomposes completely at constant temperature, with the simultaneous precipitation of ferrite and cementite in the form of pearlite. Below the eutectoid temperature the alloy consists entirely of pearlite, and no further phase change occurs on cooling to room temperature.

Alloy *O* contains 1.3 per cent carbon and is typical of alloys having carbon contents between that of the eutectoid and that of saturated austenite at the eutectic temperature, that is, between 0.90 and 1.7 per cent. From the commercial standpoint, it is a tool steel a little above the average in carbon. Solidification begins at the point 9, with the separation of primary austenite, and ends at the point 10, where the alloy consists entirely of austenite. On cooling to point 11, pro-eutectoid cementite begins to precipitate and increases in quantity as the alloy cools to the eutectoid temperature. This precipitation of cementite reduces the carbon content of the austenite, which reaches eutectoid composition when the alloy

has cooled to the eutectoid temperature. Here, at the point 12, the residual austenite changes at constant temperature to pearlite. The alloy, now consisting of pearlite and cementite, cools to room temperature without further phase change.

Alloy *P* contains 1.7 per cent carbon, which is the maximum amount soluble in iron in the solid state. Austenite begins to freeze out of the melt at the point 13, and continues down to the point *E*, where solidification is complete and the alloy consists entirely of saturated austenite. On further cooling, cementite immediately begins to precipitate and continues according to the solubility curve, *SE*. At the point 14 the austenite has reached the eutectoid composition and is converted to pearlite. The alloy is now made up of pearlite and the greatest possible amount of pro-eutectoid cementite. The total cementite in the

alloy is $\frac{1.7}{6.67} \times 100 = 25.5$ per cent. This leaves 74.5 per cent of iron, which is found entirely in the pearlite. Associated with this iron in the pearlite is 11.5 per cent cementite. The remainder of the cementite, 14 per cent, is present as pro-eutectoid cementite. The alloy contains 86 per cent pearlite.

Alloy *R* contains 2.4 per cent carbon and is representative of alloys containing 1.7 to 4.3 per cent carbon. These alloys comprise the cast-iron group, the particular alloy selected being typical of the white or hard iron castings from which malleable castings are made by annealing. Freezing begins at the point 15, with the separation of primary austenite which continues to freeze out down to the point 16, or the eutectic temperature. The melt has meanwhile been getting progressively richer in carbon, and at the point 16 solidifies entirely at constant temperature, forming the eutectic mixture of austenite and cementite. The austenite of the eutectic is saturated austenite containing 1.7 per cent carbon, and, on further cooling, this austenite, as well as the primary austenite, undergoes exactly the same changes as the alloy *P* just described, which consisted entirely of austenite of this carbon content. The final structural composition of the alloy may be calculated as follows :

The point of zero eutectic is 1.7 per cent carbon and the point of 100 per cent eutectic is 4.3 per cent carbon. The range is $4.3 - 1.7 = 2.6$ units. The alloy in question contains 2.4 per cent carbon, which is $2.4 - 1.7 = 0.7$ units from the point of zero eutectic. The per cent eutectic is, then,

$$\frac{0.7}{2.6} \times 100 = 27 \text{ per cent.}$$

$$100 - 27 = 73 \text{ per cent primary austenite.}$$

The eutectic consists, as shown above, of 52 per cent cementite and 48 per cent austenite, at the eutectic temperature. The 27 parts of eutectic in the alloy under consideration therefore contain $27 \times \frac{48}{52} = 13$ per cent austenite and 14 per cent cementite.

All the austenite, amounting to $73 + 13 = 86$ per cent, produces, on cooling to the eutectoid temperature, an amount of pro-eutectoid cementite equal to 14 per cent of its own weight, or $\frac{14}{100} \times 86 = 12$ per cent.

The remainder of the austenite, $86 - 22$, or 74 per cent of the total alloy, becomes pearlite. The final result may be summarized:

	PER CENT
Pearlite	74
Pro-eutectoid cementite	12
Eutectic cementite	14
Total	100

Iron-graphite.—Under certain conditions the carbon of iron-carbon alloys is found in the form of graphite. The graphitic form is favored by prolonged annealing and slow cooling, conditions which, in general, assist in the establishment of true equilibrium. Accordingly, it is commonly considered that iron and graphite are the ultimate stable phases of the iron-carbon system, the equilibria between iron and cementite being considered metastable. The iron-graphite system and the iron-cementite system are referred to as “the stable system” and “the metastable system” respectively.

Carbon not in the graphitic form is commonly distinguished by the term *combined carbon*. In the analysis of cast irons it is usual to determine the total carbon and the graphitic carbon, and to report the difference as combined carbon. The graphite formed in the annealing of malleable castings differs in form, although not in crystalline structure from the graphite of gray cast irons, as will be pointed out later, and is often referred to as *temper carbon*, or, in England, as *annealing carbon*. The term “combined carbon” is somewhat objectionable from the theo-

retical standpoint, as it implies that all of the carbon not in the graphitic form is in chemical combination, which is not necessarily the case. In particular, some of the carbon may be present in solid solution in the iron, in which case it is probably in a state of atomic dispersion. For carbon not in the graphitic form Howe has suggested the general term *agraphitic carbon*, which carries no implication as to its condition. The change from agraphitic or combined carbon to graphitic carbon is called *graphitization*.

The impurities that are regularly found in iron-carbon alloys exert an important and often controlling influence on the manner of occurrence of the carbon. The graphitic form is strongly favored by silicon and opposed by sulphur, when present as iron sulphide. Manganese counteracts sulphur by combining with it to form manganese sulphide, and to this extent favors graphitization. Further amounts of manganese oppose graphitization. The formation of graphitic carbon is also opposed by chromium and favored by aluminum and nickel. Phosphorus has little effect. For any composition of alloy with respect to elements other than carbon and iron, graphitization takes place more easily the higher the carbon content.

Nearly pure iron-carbon alloys do not graphitize readily and it is possible that graphite would not form at all in strictly pure alloys. If this is true, then the iron-cementite system is the stable system and the iron-graphite system is a complex one, depending on the presence of one or more other elements, such as silicon. In the present stage of knowledge, this view must be recognized as a possibility. The present discussion will, however, be based upon the more generally accepted conception of a stable iron-graphite system and a metastable iron-cementite system.

The relations of the stable and metastable iron-carbon systems are perhaps nowhere of more importance and nowhere better exemplified than in the production of American "blackheart" malleable castings. The iron of the malleable foundry contains, when ready for pouring, from 2 to 3 per cent of carbon, and an amount of silicon (0.4 to 1.2 per cent) such that, when cast in the usual green sand molds, the resulting castings will be white or hard throughout, *i.e.*, will contain no graphitic carbon, but will graphitize on suitable annealing. The phase changes taking place during the solidification and subsequent cooling of such an alloy have been discussed above, an alloy containing 2.4 per cent

carbon having been selected as an example. The final structural composition of this alloy was also calculated and summarized as follows:

	PER CENT
Pearlite.....	74
Pro-eutectoid cementite.....	12
Eutectic cementite.....	14

The hardness and brittleness of the original casting are due to the large quantity of the hard and brittle cementite, and to its commanding position in the structure of the alloy. The hard iron castings are made "malleable" and ductile by a long annealing process, the essential function of which is the conversion of substantially all of the combined carbon to graphitic carbon.

Suppose some pieces of the white or hard iron to be heated to a temperature between the eutectoid and eutectic temperatures of the iron-cementite system, say, about 900° C. The formation of the graphite will soon begin and the progress of the conversion can be followed quantitatively by quenching specimens at intervals and determining their content of combined carbon. It will be found that the combined carbon content decreases as the annealing is continued, but that finally a constant value (about 1.0 per cent) is reached which cannot be further decreased, no matter how long the annealing. At the annealing temperature this "combined carbon" is entirely in solution in the iron. All free cementite has disappeared and the alloy contains only two phases, austenite and graphite. This is an equilibrium condition of the iron-graphite system.

If this procedure is repeated at various temperatures between those of the eutectic and eutectoid transformations, a definite equilibrium value of combined carbon will be obtained for each temperature. In each case this value represents the carbon concentration in the austenite at the time of quenching. The carbon concentration of an austenitic solid solution in equilibrium with graphitic carbon may be quite correctly referred to as the *solubility* of graphite. This expression does not carry any implication as to the constitution of the solid solution. Graphite is a definite crystalline form of carbon, depending for its identity upon a definite and fairly complex arrangement of carbon atoms. This arrangement cannot be preserved in the solid solution in iron.

The solubility of graphite in iron, as determined by the method just outlined, increases with increasing temperature throughout

the range between the eutectoid temperature and the eutectic temperature. If the annealing is carried out slightly below the eutectoid temperature, the combined carbon content of the iron will ultimately be reduced very nearly to zero. That is, below the eutectoid temperature the solubility of graphite in iron is very slight, probably less than 0.05 per cent. There is an abrupt change in solubility at the eutectoid temperature. In the practical annealing of malleable castings, the greater part of the graphitization is brought about above the eutectoid temperature (that is, at about 800 to 900° C.). The final complete graphitization is secured by cooling very slowly through the eutectoid temperature and the range immediately below that temperature. Complete graphitization can occur only below the eutectoid temperature.

It will be evident from this discussion that the solubility of graphite in iron at various temperatures corresponds closely with that of cementite. Theoretical considerations indicate that at any given temperature the solubility of graphite is less than that of cementite. Experimental results tend to confirm this indication, although it is difficult to determine the actual relationships accurately. The equilibria of the iron-graphite system are not readily attainable, except in the presence of considerable quantities of silicon. This silicon probably alters the solubility of cementite in iron in a manner which is not easily determined because of the tendency of the alloy to graphitize. In other words, the graphite solubility curves are not accurately known for pure iron-carbon alloys, nor the cementite solubility curves for iron-carbon alloys containing considerable quantities of silicon. In fact, the graphite solubility curves have not been determined for any alloys with the accuracy which is desirable in constitutional work of such importance.

Five different phases are encountered in the two systems: (1) liquid solution; (2) austenitic solid solution; (3) ferrite, the very dilute solid solution in Alpha iron; (4) graphite; and (5) cementite. The first three of these phases are common to the two systems.

The identity of the two austenitic solid solutions has been questioned,¹ the hypothesis being advanced that the constitution

¹ SCHWARTZ, PAYNE, GASTON and AUSTIN, "Conditions of Stable Equilibrium in Iron-carbon Alloys," American Institute of Mining Engineers, vol. 68, 1923, p. 916.

of the solid solution in equilibrium with cementite is different from that of the solid solution in equilibrium with graphite. The suggested difference is in the manner of distribution of the carbon. At the present state of knowledge, this hypothesis is theoretically admissible, as well as the corresponding ideas that the liquid phases and Alpha iron solid solutions of the two systems differ in constitution. It seems very probable, however, that this is not the case, but that the three phases mentioned are identical in

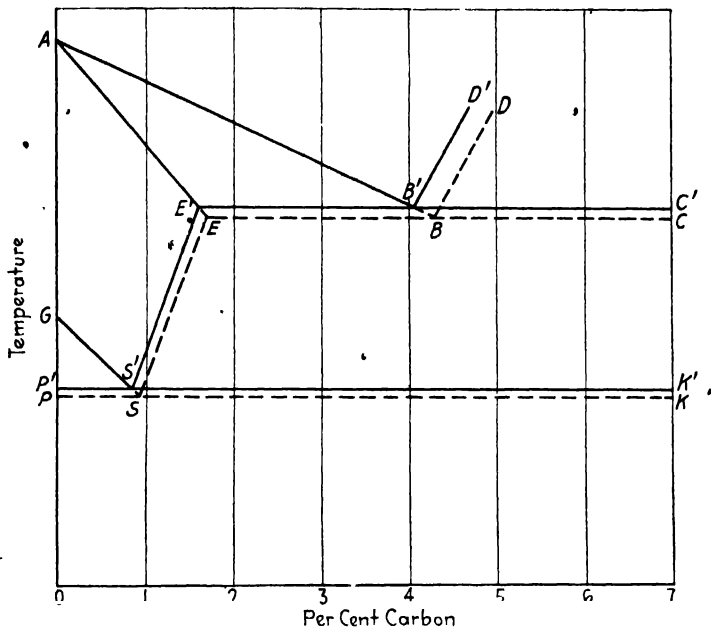


FIG. 110.—Constitution diagram of the iron-graphite system.

constitution, whether the phase with which they are in equilibrium is cementite or graphite.

The relations between the stable and metastable systems are shown qualitatively in Fig. 110. The full lines represent the equilibria of the iron-graphite system, while the dotted lines represent the iron-cementite system. Where only a single full line is shown, the two diagrams coincide. These single lines AB , AE , and GS , represent equilibria between those three phases which are common to the two systems and, granting that the constitution of these phases is the same for each system, the lines representing

their mutual solubility relations must be the same. The lines are extended into the regions of metastable equilibrium without change of direction, in accordance with observations on other systems susceptible to exact measurements. It has been mentioned above, for example, that the vapor pressure curve of under-cooled water is a continuation of the normal vapor pressure curve as determined above the freezing point.

The eutectic lines, $E'C'$ and EC , must be drawn horizontal, and hence parallel, since the eutectic transformation takes place at constant temperature throughout each system. The same is true of $P'K'$ and PK . The lines $B'D'$ and BD , representing the solubilities of graphite and cementite respectively in the liquid, are not necessarily parallel, nor are the lines $S'E'$ and SE , representing the solubilities of graphite and cementite respectively in austenite.

Consider the significance of the various lines and fields of the iron-graphite diagram, confining the attention for the moment to the full lines of Fig. 110. Above the liquidus $AB'D'$ all alloys are completely molten. On cooling to AB' , solidification begins with the separation of primary austenite, as in the metastable system. Alloys richer in carbon begin to freeze on cooling to $B'D'$, if the cooling is sufficiently slow to produce stable equilibrium. The solid phase in this case is graphite. Excess graphite commonly separates out from molten high-silicon pig iron and, because of its lightness, comes to the surface and escapes as "kish." The point B' is the eutectic point of the stable system where, under equilibrium conditions, austenite and graphite separate simultaneously from the melt.

Within the field $AB'E'$, solid austenite is in equilibrium with liquid. Within the area $D'B'C'$, the stable phases are graphite and liquid. All alloys containing more carbon than represented by the point E' are partly liquid when cooled to the line $E'C'$. This remaining liquid, which has the composition of the iron-graphite eutectic, then solidifies at constant temperature. It will be noted that the carbon content of the iron-graphite eutectic is less than that of the iron-cementite eutectic.

Within the area $AE'S'G$ only one phase, austenite, is present. On cooling to the line GS' , alloys containing less carbon than represented by the point S' begin to precipitate ferrite, exactly as in the metastable system. No graphite can be formed in these alloys until the line $P'S'$ is reached. Austenite containing

more carbon than represented by the point S' begins to deposit graphite on cooling very slowly to the line $S'E'$, the graphite solubility curve. The austenite is gradually depleted in carbon and reaches the eutectoid temperature, $P'S'K'$, with a carbon content represented by the point S' . The austenite of the hypo-eutectoid alloys is correspondingly enriched in carbon by the precipitation of ferrite and likewise reaches $P'S'K'$ with a carbon content represented by the point S' . This residual austenite of eutectoid composition then decomposes at constant temperature into a mixture of graphite and ferrite nearly free from carbon, provided the necessary conditions obtain as to rate of cooling and the presence of contributory elements, such as silicon.

The term "eutectoid", scarcely has the same significance in the stable system that it has in the metastable system. With ordinary amounts of silicon present, the rate of cooling necessary to cause complete decomposition of the austenite to ferrite and graphite at the eutectoid temperature is so extremely slow that it is practically never realized. Taking malleable castings again as an example, suppose a piece of hard iron has been annealed at 900°C . until it is in a state of equilibrium, that is, until it consists entirely of austenite and graphite. It will not then require an impracticably slow rate of cooling to allow this equilibrium to be maintained on cooling to the eutectoid temperature. Suppose that a rate of cooling is employed which will maintain the equilibrium of the stable system, so that the decreasingly soluble carbon of the austenite will precipitate as graphite instead of cementite. On reaching the eutectoid temperature of the iron-graphite system, $P'S'K'$, the solubility of graphite suddenly decreases almost to zero. With any ordinary rate of cooling, however, there is not time for all of the carbon of the austenite to deposit as graphite. The remaining undecomposed austenite undercools to PSK , and then breaks down largely into pearlite, the eutectoid of the metastable system. The conversion of this combined carbon to graphitic carbon takes place during the slow cooling immediately below the eutectoid temperature of the metastable system. There is, therefore, no eutectoid structure formed by the sudden and complete, simultaneous precipitation of ferrite and graphite.

When a hypo-eutectoid steel is cooled slowly through the thermal critical range, ferrite precipitates from GS to PS , and the residual austenite breaks down to pearlite at PSK . Even in

the presence of considerable quantities of silicon, graphite is seldom formed in hypo-eutectoid alloys. There can be no graphite particles formed at higher temperatures to act as nuclei and encourage graphitization at the eutectoid temperature. The "iron-graphite eutectoid," therefore, has little meaning in hypo-eutectoid alloys.

Although the significance of the iron-graphite eutectoid is thus limited, its meaning is quite definite as applied to the composition and temperature limits of graphitization. The eutectoid temperature of the stable system is a definite temperature at which there is an abrupt and marked change in the solubility of graphite in iron. Above this temperature it is impossible to obtain complete graphitization, but below this temperature graphitization can be carried so far toward completion that the remaining content of combined carbon is less than 0.05 per cent.

As mentioned above, the solubility of graphite is theoretically less than that of cementite at any given temperature, according to the general proposition that the solubility of a stable phase is less than that of a metastable phase in the same solvent. The actual differences in solubility at various temperatures are not accurately known, nor is the difference in the carbon content of the two eutectoids. There has been considerable controversy in regard to the latter point, some writers claiming that the iron-graphite eutectoid lay at nearly zero per cent of carbon. Recent work has shown that the carbon content is certainly very appreciable, a value of 0.53 per cent having been found for an iron containing approximately 1.0 per cent silicon.¹ The same investigators found the eutectoid temperature of the iron-graphite system to lie less than 10° C. above that of the metastable system.

If it is assumed that the austenite solid solutions of the two systems are identical in constitution, then the line GS is the same for both the systems as drawn, and the eutectoid point S' is fixed by the intersection of GS with the eutectoid horizontal, PK . Now if GS passes into the metastable region without marked change of slope, and if $P'K'$ is less than 10° C. above PK , then the carbon content of the iron-graphite eutectoid cannot be more than about 0.05 per cent less than that of the iron-cementite eutectoid. The carbon content of the iron-cementite eutectoid, which is about 0.90 per cent in the pure iron-carbon alloys, may have a somewhat different value in the alloys containing 1.0 per cent

¹ SCHWARTZ, PAYNE, GASTON, and AUSTIN, *Op cit.*

silicon, but is probably at least 0.70 per cent. The above reasoning would then indicate that the iron-graphite eutectoid in the same alloy contains at least 0.65 per cent carbon. In other words, a eutectoid ratio of 0.53 per cent carbon is not consistent with the close proximity of the two eutectoid temperatures, unless the very improbable view is adopted that the austenitic solid solutions of the two systems differ in constitution. In general, it seems that the graphite solubility curves are quite close to the cementite solubility curves.

It is of practical interest, and perhaps of some assistance in understanding the relations of the stable and metastable systems, to point out the reversibility of the graphitization process. If a completely graphitized malleable casting is reheated to about 900° C., some of the graphite will go into solution, and, if the time of heating is sufficient, the carbon content of the austenite so formed will reach the value indicated by the solubility curve, $S'E'$. If the alloy is then quenched, it will be hardened and this amount of carbon will be found in the "combined" form. Air cooling from 900° C. will permit a small amount of graphitization, but most of the dissolved carbon will be found as cementite (in pearlite).

Copper-zinc.—Six solid phases are found in the copper-zinc alloy system, usually designated by the letters Alpha, Beta, Gamma, Delta, Zeta, and Eta. The present discussion will be confined to alloys containing less than 60 per cent zinc. This group comprises all of the useful copper-rich alloys, or brasses. The Alpha phase is a solid solution containing up to 36 per cent zinc, and is the only structural constituent of the most ductile brasses, such as those used for cartridge cases and condenser tubes, which contain 30 to 33 per cent zinc. The Beta phase is also a solid solution, but is somewhat harder and less ductile than Alpha brass. Alloys containing the Beta phase seem to be the best adapted for hot working, however. The Gamma phase is quite hard and brittle, and alloys containing even small quantities of it are unfit for mechanical purposes. It has been regarded both as a solid solution and as a definite intermetallic compound represented by the formula Cu_2Zn_3 . The inner structures of various phases of the copper-zinc system have been discussed in the preceding chapter.

The constitution diagram of the system is shown in Fig. 111. Above the liquidus CID the alloys are completely molten.

Solidification is complete on passing the solidus *CABED*. The regions of stability of the solid Alpha, Beta, and Gamma phases are indicated in the diagram.

Alloys to the left of the point *A* solidify in the manner typical of solid solutions, as described in detail in connection with the copper-nickel system. On cooling to the line *CI*, the Alpha solid solution begins to form, and solidification is complete on reaching *CA*.

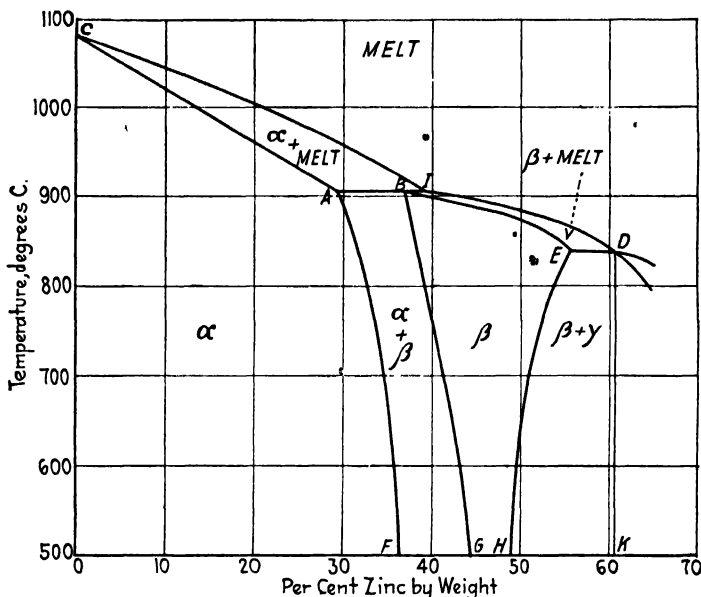


FIG. 111.—Constitution diagram of the copper-zinc alloys.

Alloys between the points *A* and *I* exhibit solidification phenomena of a type not previously described. Freezing begins with the separation of the Alpha solid solution at the line *CI*. The Alpha phase continues to freeze out until the alloy cools to the temperature represented by the horizontal *ABI* (905° C.). At this temperature the solid Alpha phase and the melt react with each other to form the Beta phase, the exact sequence of events depending on the composition of the alloy.

In alloys between *A* and *B* there is an excess of the Alpha phase, and the liquid is completely used up in the reaction. Solidification is complete on passing the line *AB*, the solid alloy consisting of the two phases, Alpha and Beta.

In alloys between *B* and *I* the melt is in excess, and the solid Alpha phase is completely used up in the reaction. At the end of the reaction the alloy consists of Beta solid solution and liquid of a composition lying to the right of point *I*. On further cooling, this liquid deposits Beta solid solution until freezing is complete at the solidus *BE*.

The alloy represented by the point *B* contains exactly enough of the Alpha phase to react completely with the liquid. On cooling just below *ABI*, the alloy is completely solid and consists entirely of the Beta phase.

The temperature at which this reaction takes place is called the *peritectic temperature*, and the reaction itself is referred to as the *peritectic reaction*. The point *B* in Fig. 111 is the *peritectic point*. When this type of reaction occurs, there are different solid phases in equilibrium with the melt above and below the peritectic temperature. During the peritectic reaction there are three phases (two solid and one liquid) in equilibrium, so that the temperature must remain constant until at least one of the phases disappears.

Copper-zinc alloys between the points *I* and *E* solidify according to the simple solid solution type. The Beta phase begins to freeze out on cooling to the liquidus *ID*, and continues to form, until at *BE* the alloy is completely solid. The line *ED* is another peritectic horizontal, and alloys whose compositions lie between the points *E* and *D* exhibit a peritectic reaction, the primary Beta phase reacting with the melt to form the Gamma phase, which, as pointed out above, is generally regarded as the compound, Cu_2Zn_3 . The peritectic point is in this case at, or very near the point *D*.

The mutual solubilities of the various solid phases change with temperature, as shown by the solubility curves, *AF*, *BG*, and *EH*. It will be noted that the solubility of zinc in the Alpha phase increases as the temperature is lowered, the value at room temperature being approximately 36 per cent. Brass containing 33 per cent zinc consists entirely of the Alpha phase at ordinary temperatures, but develops some Beta on heating above about 800° C. Muntz metal, which contains about 40 per cent zinc, is normally a mixture of Alpha and Beta, but becomes homogeneous Beta on annealing above *BG*.

Alloys containing the Beta phase show a heat effect at about 470° C., the cause of which has been the subject of considerable

investigation and discussion. It has been suggested that at this temperature the Beta phase breaks up, on cooling, into a eutectoid mixture of Alpha and Gamma. Alloys containing about 47 per cent zinc apparently consist of a single homogeneous solid solution after cooling to room temperature. Carpenter and Edwards¹ suggested that this "apparent Beta" consists in reality of a submicroscopic mixture of Alpha and Gamma. Hudson² and others have considered that the heat effect is due to a polymorphic transformation of the Beta constituent. This view is more consistent with the thermal data of Hatch,³ which show that the transformation temperature remains constant at about 465° C. through the Alpha and Beta field of the diagram, but rises about 12° C. on passing from left to right through the field of homogeneous Beta, again remaining constant at about 477° C. through the field of Beta and Gamma. A eutectoid inversion should take place at constant temperature throughout the Beta field. Finally, such work as has been done by the *x*-ray method of crystal analysis indicates that apparent Beta contains only one space lattice, the body-centered cubic, and is, therefore, a single phase rather than a mixture. The problem is capable of solution by the *x*-ray method, but there appears to be a need for some further investigation. It is because of the questionable nature of this transformation that the diagram in Fig. 111 has been discontinued at 500° C.

Aluminum-silicon.—It has already been mentioned that slight departures from true equilibrium are frequent and even to be expected when certain alloys freeze. A very remarkable case of undercooling and accompanying change in constitution is found in the aluminum-silicon alloy system. The solid lines in Fig. 112 represent the normal equilibrium of these alloys. When some metallic sodium is present, the results represented by the dotted lines can be obtained, even with relatively slow cooling. The freezing point of the eutectic is lowered and the amount of silicon in the eutectic is increased, due to the presence of the sodium.

This abnormal occurrence seems to be due to the obstructing action of the sodium particles on the crystallization of the silicon.

¹ CARPENTER and EDWARDS, *J. Inst. Metals*, No. 1, p. 127, 1911.

² HUDSON, *J. Inst. Metals*, No. 2, p. 89, 1914.

³ MATHEWSON and DAVIDSON, "Metallography of Brass," *J. Am. Inst. Metals*, vol. 11, No. 1.

Both the excess silicon and the eutectic silicon crystallization are affected. The alloy containing 13 per cent silicon should normally begin to freeze out excess silicon at a temperature near 600° C. If the alloy contains a few hundredths of 1 per cent of sodium, the beginning of freezing may be below 570° C. and the first material to freeze is nearly pure aluminum instead of silicon. As cooling continues, the liquid alloy concentrates in silicon until composition *b* is reached, when the eutectic freezes. The normal 13 per cent silicon alloy consists, after solidification, of excess silicon and eutectic. The eutectic contains about 11 per cent silicon and 89 per cent aluminum. The silicon is in relatively large plates if the alloy has been cooled slowly, as, for

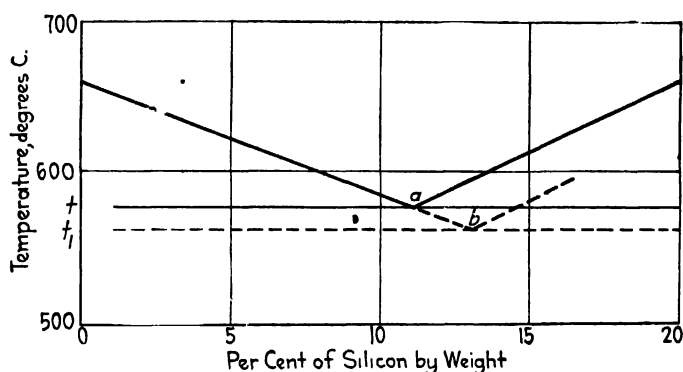


FIG. 112.—Constitution diagram of the aluminum-silicon alloys.

example, in sand castings. The aluminum-silicon alloys to which sodium has been added are called “modified” alloys, whereas those to which no sodium has been added are called “normal” alloys. The modified alloys may depart only slightly from the normal alloys as regards the composition of the eutectic and quantity and kind of excess substance, when a small quantity of sodium is added. The larger the quantity of sodium up to a certain limit, the greater the departure from the normal. The maximum departure obtainable seems to be reached when the eutectic contains nearly 15 per cent silicon. The silicon in the eutectic of the modified alloys is much more finely dispersed than in the normal alloys. The refinement of structure imparts to the modified alloys high strength and ductility as compared to the normal alloys of the same silicon content.

It has been suggested that the sodium enters into the alloy with the resultant formation of a ternary eutectic containing aluminum, silicon, and sodium. The authors believe, however, that the action of the sodium is one of obstruction to crystallization. This view is supported by the following considerations:

1. The abnormality occurs only on freezing, *i.e.*, no matter how much the modified alloy departs from the equilibrium of the normal alloys during and after freezing, normality obtains on melting. The freezing point of the eutectic may be 565°C. , but its melting point in the same alloy will be 577°C. This shows that the sodium does not materially disturb the true equilibrium.

2. In aluminum-silicon alloys, in which excess aluminum separates on cooling, the beginning of freezing occurs at the same temperature, whether the alloys are modified or not. This shows that the presence of the sodium has no influence on the temperature of separation of aluminum itself.

3. When modified alloys are remelted and allowed to stand in the molten state a short time and then resolidified, they revert to the normal state. This is due to the rapid elimination of the sodium. In fact, this elimination of sodium is so rapid as practically to preclude the possibility of its existence in solution in the aluminum. The rate is suggestive of small globules of sodium rising in the aluminum by virtue of the low density of the former.

4. An effect somewhat similar to that produced by sodium can be produced by causing solidification to take place rapidly, as in a metal mold. Also, with a very small amount of sodium, the effect of rapid solidification produces a greater departure from equilibrium than slow cooling.

5. The addition of sodium, in gradually increasing amounts, to an aluminum-copper alloy containing 4 per cent copper causes a series of changes in the grain size similar to the known action of small discrete particles (refer to Chap. V).

From the above considerations it seems probable that a small quantity of sodium goes into true solution in the molten alloy at high temperatures, and mostly separates in the form of small liquid globules during cooling and before the solidification of the constituents of the alloy itself. The crystallization of the silicon, especially, is interfered with by these sodium globules. The departure from equilibrium is entirely in the direction of delayed crystallization of silicon, whether it be excess or eutectic

silicon, the aluminum behaving normally as regards temperature of crystallization. The finer structure of the eutectic in modified alloys is to be partly ascribed to the obstructing effect of the sodium globules and partly to the rapid formation of silicon nuclei in the undercooled, supersaturated liquid alloy.

Determination of Alloy Constitution.—The meaning and the degree of reliability of the diagrams of alloy constitution can be best evaluated in the light of a knowledge of how these diagrams are obtained. It is beyond the scope of this work to give a complete discussion or working knowledge of this subject, but the more important methods will be briefly outlined and the present state of information indicated.

The problem is that of determining structures at various temperatures. At room temperature, direct examination is practicable both by the microscope and by the *x*-ray method. At higher temperatures, the microscope can scarcely be employed; the *x*-ray method of crystal analysis is possible, though somewhat difficult. The technique of this method will probably be developed for high-temperature work. Generally, the structures of alloys at the higher temperatures are investigated by less direct means.

A fundamental distinction is to be made between methods which may be classed as static and others which may be classed as dynamic. When the structure of an alloy is examined at a given temperature after being heated at that temperature until it is believed that phase equilibrium has been completely established, the method may be described as "static." If it is impracticable to examine the specimen at the temperature in question, it may be cooled rapidly, as by quenching, and examined at room temperature. It is then assumed that the structure stable at the high temperature has been preserved by the rapid cooling, or that it has undergone change in a manner so well understood that the original high-temperature condition can be deduced. The method is still static, in that the alloy was brought to a state of phase equilibrium at the temperature under investigation. If, on the other hand, it is sought to detect phase changes by heat effects or other discontinuous physical changes on falling or rising temperatures, the method may be described as "dynamic."

Mention has been made above of the lag in the attainment of phase equilibrium, particularly in the solid state. Hence, the

temperature of a phase change, as indicated by an observed discontinuity on cooling or heating, may not be the temperature corresponding to conditions of true equilibrium.

The construction of the equilibrium diagram consists of three principal tasks: the determination of (1) the liquidus, (2) the solidus, and (3) the curves of solid solubility. The general methods employed for these purposes are now fairly standard, although the details vary in different cases, and special methods are often necessary.

The liquidus is generally determined by means of cooling curves. The first separation of solid from the melt is marked by a retardation of the normal rate of cooling. The temperature to be taken is that corresponding to the beginning of the thermal arrest. The possibility of undercooling must not be overlooked, as the melt may cool considerably below the true liquidus before solidification begins. The overheating of a solid has never been observed, and for this reason it has often been urged that heating curves give more reliable information than cooling curves. The beginning of a transformation is always more sharply marked, however, than the end of a transformation, and for this and other reasons the cooling curve is generally preferred. Undercooling can usually be prevented by stirring the melt or by inoculating with some of the solid phase. Any such disturbance of normal cooling conditions should, however, be avoided if possible. There is sometimes danger of failing to detect, by the cooling curve, the first separation of a solid phase from the melt, when such separation is accompanied by only a slight evolution of heat.

The preferred method for the determination of the solidus consists in quenching specimens of the alloy under investigation from a series of temperatures near the solidus, and observing the microstructures after quenching. Consider, for example, an aluminum-copper alloy containing 3 per cent copper. Specimens of the alloy are prepared in a condition as uniform as possible, preferably by hot working and thorough annealing at a temperature sufficient for the complete solution and thorough diffusion of the copper, say, about 500° C. Suppose the temperature of the solidus, that is, of incipient fusion, for this alloy is 595° C. Then a specimen may be heated indefinitely at a lower temperature, as at 585° C., without change of state. If quenched from this temperature and examined with the microscope, it will show the aggregate of polyhedral grains characteristic of a

homogeneous solid solution. Another specimen heated at a temperature slightly above the solidus, say at 605° C., and quenched will show an entirely different appearance. Areas which appear dark after etching, and which are, in reality, complex in structure, are observed around the grains and as spots within the grains. These areas represent portions of the alloy which were molten at the time of quenching. It is obvious how the solidus can be located by the examination of a series of such specimens. In general, it is essential that the solid alloy be in a state of phase equilibrium at temperatures just below the solidus. For the actual experiments, it is desirable to have a furnace whose temperature is automatically controlled within a narrow range of temperature. The better the control, the more closely can the temperature in question be determined. A common difficulty in the application of this method is due to a change in the composition of the alloy during heating, by the volatilization of one of its components. This occurs in the case of the iron-carbon alloys and the copper-zinc alloys.

It is only very recently that the importance of accurate determinations of solid solubilities has been adequately realized. Formerly, attention was concentrated on the liquidus, and there was a general disposition to neglect solid solubility relations as unimportant. In particular, there was a tendency to assume that a solubility value as determined approximately at some high temperature remained practically unchanged down to room temperature. Recent work has shown that this is perhaps seldom the case, and that important changes in the physical properties of alloys can often be brought about by heat treatments based on changes in solid solubilities with change in temperature.

The method for the establishment of curves of solid solubilities consists in the prolonged annealing, at definite temperatures, of specimens of selected composition, followed by quenching and microscopic examination for the presence or absence of the phase in question. The success of the method requires the establishment of complete phase equilibrium at the temperature of annealing, and the obtaining of the heterogeneous structures in a form coarse enough for resolution by the microscope. This is, in general, best accomplished by approaching the temperature of the experiment slowly from a higher temperature. Consider, for example, an aluminum-copper alloy containing 3.5 per cent copper. This amount of copper dissolves completely in aluminum

at about 500° C. Suppose it is desired to determine whether or not 3.5 per cent of copper will dissolve in aluminum at 300° C. If a specimen of the alloy is cooled very slowly from 500 to 300° C., held for a time to insure equilibrium, and quenched, it will be found to contain some precipitated CuAl_2 in the form of particles large enough to be seen with the microscope. If, on the other hand, the alloy had been quenched from 500° C. and then reheated to 300° C., even for a very long time, the same amount of CuAl_2 would have been precipitated, but in the form of particles too small to be seen with the microscope.

In some cases it may be impossible to obtain a precipitate coarse enough for microscopic observation. This is particularly apt to be the case when the precipitate begins to form at low temperatures, where particle growth is very slow and perhaps definitely limited. The presence of such submicroscopic precipitates can then sometimes be inferred from their remarkable effects on the physical properties of the alloy. These effects will be described fully in Chap. X, particularly in connection with the "age hardening" of aluminum alloys.

Other methods may be available for the detection and identification of a phase which is present in the form of particles too small to be seen with the microscope. Such particles are crystalline in structure, and give characteristic patterns with the *x*-ray spectrometer, even when exceedingly small in size. The *x*-ray method is at present, however, limited in its sensitivity. If an alloy contained 3 per cent by volume of a certain phase, for example, the *x*-ray might fail entirely to show the presence of this phase.

Magnetic analysis has been applied to the detection of cementite in steel. Cementite undergoes a sharp change in magnetic susceptibility at about 215° C. If sufficient cementite is present, even in the form of particles of submicroscopic size, the alloy, as a whole, will show an observable discontinuity on being heated through 215° C.

Phase changes within an alloy are accompanied by changes or discontinuities in all of the physical properties, some of which may be suitable for observation. Some of the properties which have been followed in investigation of alloy constitution are density, electrical conductivity, thermoelectromotive force, etc.

Mention should be made of a certain method of thermal analysis developed chiefly by Tammann and largely employed by

German and other Continental investigators. The method consists in the quantitative application of the data derived from cooling curves. The quantity of heat evolved by a given phase change is proportional to the amount of material participating in that change. The quantity of heat evolved is indicated by the duration of the thermal arrest or "halt" on cooling, if the conditions of experiment are kept constant. Suppose, for example, that two alloys of a eutectiferous series, such as the lead-antimony series, are dealt with; starting with identical amounts of the two alloys, heating each to the same initial temperature, and cooling

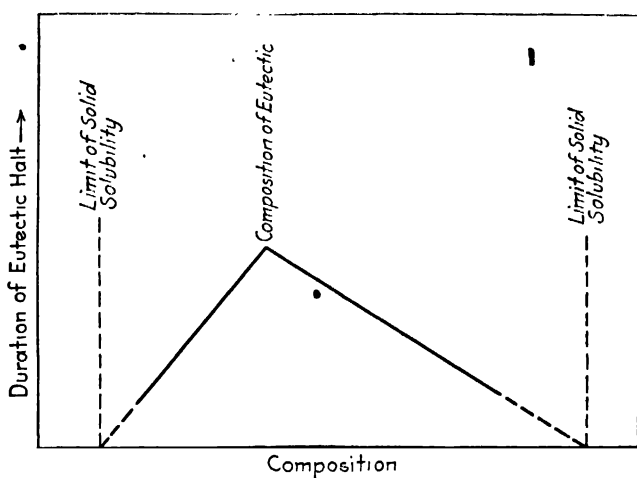


FIG. 113.—Curve of eutectic halts.

under similar thermal conditions, then the periods of the eutectic halts should be proportional to the quantities of heat evolved and, therefore, to the quantities of eutectic in the alloys. If the durations of the eutectic halt were thus determined for alloys throughout the series, and plotted against the composition, the result would be a curve rising from zero at the lead end of the series to a maximum at the composition of the eutectic (13 per cent antimony) and falling again at a linear rate to zero at the antimony end.

One of the most common applications of this method has been in the fixing of the ends of the eutectic horizontals. In systems showing partial solid solubility, like the silver-copper system, the eutectic horizontal terminates at points which indicate the compo-

sitions of the solid solution phases at the eutectic temperature. The locations of these points are found by plotting the eutectic halts and extrapolating to zero duration (see Fig. 113).

The Tammann method is open to objections which have discredited it for exact work, although it is undoubtedly useful in a qualitative way. Among these objections may be mentioned the practical difficulty of duplicating the conditions of cooling in successive experiments, and the fact that alloys seldom attain conditions of equilibrium during cooling at the rates which must be employed in taking cooling curves.

The extent of present knowledge of the possible binary alloy systems is very limited, although the information is fairly complete regarding those of greatest commercial importance. If it is considered that there are about 60 metallic elements, then there are about 3,500 binary combinations theoretically possible. Some of these will, of course, be excluded because of the immiscibility or volatility of the components. Only a few hundred have been investigated, and most of these only in a cursory manner. Probably most of the investigations are due to the German schools, and fail because of both object and method to give the information now desired. The object of many of these studies was merely the determination of the intermetallic compounds of a series. The methods employed were often unsatisfactory as to purity of material, quantities used, accuracy and sensitivity of temperature measurements, and soundness of conception. The investigation of alloy constitution has now been carried to a much higher and more exact stage of development, best exemplified perhaps in the work of the National Physical Laboratory of Great Britain, and completely described in the publications from that institution. In general, it may be said that the earlier results are often incomplete, as well as sometimes inaccurate, and that on more detailed study many systems appear more complex than was thought at first. This applies, in particular, to the changes in the solid state which were frequently neglected in the earlier work. Finally, it must be considered that the determination of alloy constitution is still a matter of experiment. No generalizations exist by means of which the constitution of an unknown system can be predicted with any confidence. Rapidly increasing knowledge of the structures and properties of atoms and of the arrangement of atoms in metals gives some promise of such generalizations.

Ternary Alloy Systems.—Many of the most important industrial alloys contain three or more essential components. At first thought, one might be tempted to conclude that most of the important alloys belong to ternary or more complex systems. Some of the recently developed alloys come to mind—high-speed steel, the alloy structural steels, duralumin—in which three or more components are necessary. A more careful consideration shows, however, that the alloys which are most important, from the standpoint of quantity and value of product, are essentially binary alloys. Most important of all are the straight carbon steels, and among the non-ferrous alloys the simple copper-zinc brasses. The most widely used aluminum alloy is probably the casting alloy containing 3 per cent copper. Many other important binary alloys come to mind, such as the lead-tin alloys used for solders and for coating terne plate; the silver-copper alloys used for coinage and “Sterling” silver ware; and the gold-copper alloys used for coinage and jewelry.

Of those alloys, the properties of which depend on the presence of three components, many can be most conveniently and most logically regarded as binary alloys whose constitution and properties are modified in degree rather than in kind by the presence of the third component. The structural nickel-steels, for example, contain usually less than 5 per cent of nickel. The effects of the nickel are fairly well understood when it is known that it enters into solid solution in the iron, that it lowers the thermal critical points, and that it retards the decomposition of the austenitic solid solutions. These alloys are regarded as essentially iron-carbon alloys, modified qualitatively by the addition of nickel.

The complete investigation of the equilibria of a ternary system is a very difficult and tedious task. If the study of a binary system requires the examination of 50 different alloys, then the study of a ternary system in similar detail requires the examination of 1,250 different alloys. Again, if the possible combinations of 60 metallic elements are considered, there are about 3,500 binary combinations and about 200,000 ternary combinations. From what has been said above of the difficulties involved in the determination of the constitution of binary alloys, and of the lack of complete information regarding any but a comparatively small number of the more important binary alloys, it will readily be apparent that existing knowledge of

ternary and more complex equilibria is almost negligible. Probably no ternary system has been investigated throughout with such completeness and exactness as some of the important binary systems.

In any particular ternary system, the alloys of practical value are generally found only within fairly limited ranges of composition. If the study of the equilibria of the system is confined to these regions, the problem is greatly simplified. Some such portions of ternary systems have recently been quite fully studied.

The graphical representation of ternary equilibria requires a three-dimensional figure. In the constitution diagram of a binary system, composition is represented along a straight base line. In a ternary system, composition involves two independently variable quantities and must be expressed by a two-dimensional figure. The method generally used depends on the geometrical principle that the sum of the perpendiculars from any point within an equilateral triangle is equal to the altitude of the triangle.

The method is illustrated by Fig. 114. The ternary system is made up of the three components, *A*, *B*, and *C*, which are represented by the vertices of the triangle *ABC*. The sides of the triangle represent the compositions of the three binary systems formed by the three components taken two at a time. The line *AB* represents the binary alloys of *A* with *B*, and so on. The ternary alloys are represented by points within the triangle.

The altitude of the triangle is taken as 100 per cent. Then the per cent of any component in an alloy represented by a point *O* within the triangle is given by the distance from this point to the side opposite the vertex which represents the component in question. The percentage of *A* in the alloy represented by the point *O* is given by the line *Oa*; the percentage of *B* by *Ob*; and the percentage of *C* by *Oc*. The sum of *Oa* + *Ob* + *Oc* is equal to the altitude of the triangle, or 100 per cent.

All points which represent alloys containing a constant percentage of a given component lie on a straight line parallel to the side of the triangle opposite the vertex representing that component. For example, all alloys containing 20 per cent of *A* are represented by a line drawn parallel to *BC* at a distance from *BC* equal to 20 per cent of the altitude of the triangle. A series of lines drawn through the triangle parallel to the three sides assists in reading compositions. The lines in Fig. 114 are drawn

at intervals of 10 per cent. It is thus seen that the point *O* represents an alloy containing 20 per cent *A*, 50 per cent *B*, and 30 per cent *C*.

Temperatures are plotted vertically, and the ternary equilibrium diagram is erected on the triangle as a base, just as the binary diagram is erected on the base line which expresses composition. The plane areas, which in the binary diagram represent phase fields, become volumes in the ternary space figure, and the lines bounding the various phase fields become surfaces in the ternary diagram. If, from various points within the base triangle, verticals are erected of heights which represent the temperatures

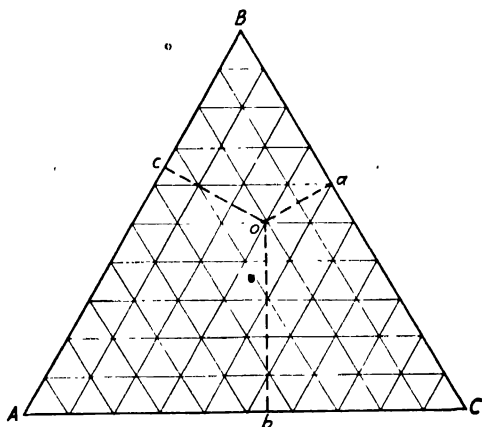


FIG. 114.—Method of plotting composition of ternary alloys.

of initial solidification of the corresponding alloys, then the ends of these verticals will determine the liquidus surface of the system. If points are located on these verticals representing the temperatures of complete solidification, or incipient fusion, of the alloys, then these points lie in and determine the solidus surface. The surfaces representing phase changes in the solid state are determined in a similar manner.

Space models representing ternary equilibria can be constructed in a number of ways. If wires are erected from the base triangle corresponding to the verticals mentioned above, and cut off at lengths representing the temperatures of initial solidification, then the ends of the wires lie in the liquidus surface. The space above the base triangle can be filled with plaster leveled off at the ends of the wires. The result is a solid triangular prism, the upper surface of which is the liquidus surface of the system.

Other surfaces can be represented by other models, but, obviously, it is not possible to represent more than one surface at a time by such models. Recently, models have been constructed entirely of wires, wires of different colors being used to represent the various surfaces, which can then all be seen and distinguished in a single model. It has been suggested that models be built of some solid but transparent material, like celluloid, in which case the various surfaces within the model could be rendered visible by thin layers of colored transparent material.

Such models are useful for demonstrating the general relations in a ternary system, but for actual application of the information plane figures are most useful. Surfaces, such as the liquidus, can be represented by contour lines, drawn at equal intervals of temperature and projected on a horizontal plane. Lines formed by the intersection of surfaces can be shown by projection on the horizontal plane. Probably the most useful of the plane figures are the vertical sections of the three-dimensional figure. These are usually taken in one of two ways. A section taken parallel to one of the sides of the triangular prism represents alloys containing a constant percentage of one of the three components. A section on a plane passing through one of the edges of the prism, that is, through one of the corners of the base triangle, represents alloys in which two of the components are present in constant relative proportions.

The possible types of ternary equilibria are many and in some cases quite complex. There will be given here only a brief and general description of the two most simple cases.

1. The three components are completely miscible in the liquid state and completely insoluble in each other in the solid state. The components taken two at a time form three binary systems of the simple eutectiferous (lead-antimony) type. The freezing points of the three binary eutectics are lowered by the addition of the third component. This results in the formation of three eutectic valleys which intersect at a point representing a ternary eutectic. At this temperature all three components freeze out simultaneously and at constant temperature.

2. The three components are completely soluble in both liquid and solid states. The liquidus and solidus are both continuous surfaces which intersect the three faces of the triangular prism in the liquidus and solidus lines of the three binary systems. The space between the two surfaces represents the region in which the alloys are partly solid and partly liquid.

CHAPTER X

STRUCTURE AND PROPERTIES OF AGGREGATES

The number of different structures possible in even a binary alloy is almost infinite, if one chooses to consider that minor variations in grain size or particle size and in the arrangement of the constituents constitute structural differences. The physical properties of any particular metallic aggregate show a correspondingly large number of gradations, which only represent, however, progressive changes between maxima and minima. The various structures are likewise, for the most part, gradual variations between certain characteristic extremes or types. In other words, the *type* of structure may remain essentially unchanged during specific changes in the proportions and arrangement of the constituents. The number of essentially different types is relatively small.

There are too many specific structures, which can be readily differentiated under the microscope or with the unaided eye, to be described in any treatise. In this chapter, therefore, there will only be considered some of the more important types of alloy structure, together with fundamental relations between structure and properties.

Some of the properties of alloys which consist of two or more constituents depend almost entirely on the specific properties of these constituents and the quantities present in the alloy, and are fairly independent of the way in which the constituents are arranged. The density of an aggregate, for example, can be calculated approximately from the densities of its structural constituents. The thermal expansivity and the elastic moduli are likewise determined principally by the nature and quantities of the structural constituents rather than by their arrangement.

Controlling Effect of Continuous Constituent.—Many properties of complex alloys depend to a greater or less extent on the arrangement of the structural constituents. The most important principle to be considered here is that the constituent which is continuous is dominant in determining the properties of the

aggregate. This can readily be seen from a consideration of the conditions illustrated schematically in Fig. 115. Suppose that the dark areas represent grains of a ductile constituent, while the white areas represent a hard and brittle constituent, such as a brittle compound. It is easily seen that the alloy, as a whole, will be brittle, because the arrangement is such that permanent deformation of the ductile constituent cannot take place without permanent deformation or rupture of the brittle constituent. Actually, rupture occurs through the brittle constituent before any considerable permanent deformation takes place.

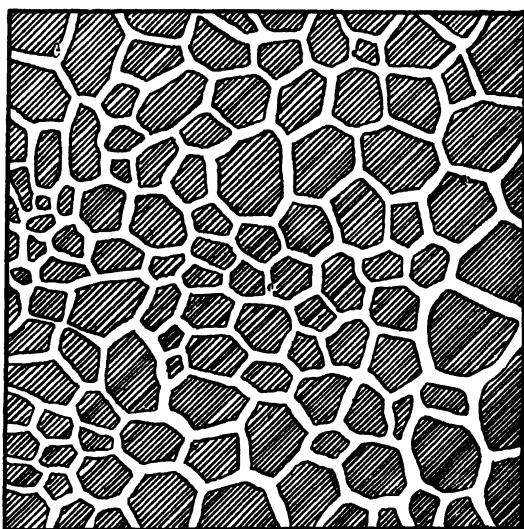


FIG. 115.—Schematic illustration of network structure.

Now suppose the conditions to be reversed, so that the dark areas represent the brittle constituent, and the white areas the ductile constituent. The alloy as a whole will then be ductile.

Electrical Properties.—In alloys which are aggregates of two or more constituents, it is a fairly general rule that the specific conductivity is a linear function of the composition by volume. That is, an alloy functions electrically as though its various constituents were grouped as continuous parallel conductors. This rule is perhaps never more than approximately true, and there are some exceptions of a very marked nature. It is obvious, for example, that an alloy which contains a constituent of very

low conductivity, in the form of a continuous network, will be a poor conductor as a whole, no matter how high the conductivity of the discontinuous constituent within the network. There is, then, a condition which is analogous to a series connection rather than a parallel connection, and the resistance of a number of conductors arranged in series is equal to the sum of the individual resistances. Even with this type of structure, however, the general rule holds approximately, if the specific conductivities of the various constituents do not differ greatly.

It is apparent also that the rule will hold more nearly when the continuous constituent is the better conductor, and that the conductivity of the alloy, as a whole, will be better. This condition is very apt to exist in alloys which have been mechanically worked, since working breaks up brittle constituents, including the dross, non-metallic compounds, and certain intermetallic compounds which are poor conductors, and establishes the continuity of the more plastic, and hence more metallic, constituent.

It seems that, in general, the electrical resistivity of an aggregate increases with the fineness of division of its constituents, and that in case of very fine subdivision the resistance may even be slightly greater than that of a solid solution of the components involved. An alloy of aluminum containing magnesium and silicon may be considered as an example. A solid solution containing up to 1.0 per cent magnesium and 0.6 per cent silicon may be formed at high temperatures and retained, in a super-saturated condition, by quenching. This solution is unstable, and on standing at ordinary temperatures, or "aging," precipitation of the compound, Mg_2Si , takes place in the form of very small particles (diameter on the order of 10^{-7} cm.) This precipitation is accompanied by a slight increase in electrical resistivity.¹ The particles of compound may be made larger by suitable heat treatment, and there is then a marked decrease in resistivity.

Taking the exceptions noted into consideration, a more accurate statement of the general rule given above may be made somewhat as follows: In alloys which are aggregates of two or more constituents, the electrical conductivity is approximately a linear function of the composition by volume, provided the various constituents do not differ greatly in conductivity, or that the best conducting constituent is continuous, and provided none

¹ EDWARDS, J. D., private communication.

of the constituents are present in the form of particles less than about 10^{-5} cm. in diameter.

Mechanical Properties.—It has been pointed out that the mechanical properties of metals and alloys fall into two general classes, which may be described by the broad terms *hardness* and *plasticity*. The plasticity of a complex alloy depends on the presence of a continuous plastic constituent. The hardness of an aggregate is determined in accordance with the principle of slip interference. Strength is, in general, proportional to hardness, but an alloy cannot be considered to be effectively strong unless it possesses at least a slight measure of plasticity and it is, therefore, a general rule that in alloys of great strength there must be a continuous plastic constituent.

Origin of Structure.—The number of constituents in an alloy and the amount of each depends largely on the chemical composition and constitution, as considered in Chap. IX. The manner in which the constituents of a given alloy are arranged is determined by the process of solidification from the molten state, phase changes in the solid state, and mechanical and thermal treatments. The results produced by these processes may be considered according to the type of alloy involved. In general, any change in the structure of an alloy brings about a change in some or all of the properties. It is often, but not always, possible to predict what change of properties will result from a given change in structure. Experience with any alloy, however, usually enables the metallographist definitely to associate certain properties with certain structures. Manufacturing processes are, therefore, often directed toward the production of certain structures because experience has taught that such structures will produce the desired combination of properties, or toward the avoidance of structures known to be undesirable.

The manner of solidification (for example, the rapidity of solidification) determines in a large measure the arrangement of the constituents. In certain cases heat treatment in the solid state is capable of changing either the proportions of constituents or the arrangement of constituents, or both. Mechanical working of an alloy often produces a profound change in structure. Below there will be described a number of typical structures of metals and alloys, considered from the standpoint of the origin of these structures.

Solidification of Solid Solutions.—A pure metal freezes or melts at a substantially constant temperature. Since only one solid phase is present, the variations in structure are in the sizes and shapes of the grains. As a rule, slow solidification produces large grains, and rapid solidification produces relatively small grains. Solid solutions containing only a small amount of solute are very similar to pure metals in their manner of solidification. As the amount of solute increases, however, freezing takes place over a greater range of temperature and there is a temporary concentration in the liquid portion of the alloy of that component whose further addition to the alloy would lower its freezing point. This process of solidification has been described in connection with the discussion of solid solution alloys in Chap. VIII and IX. The segregation of the solid solution alloy into portions having different chemical compositions is sometimes temporary because diffusion takes place after solidification and, when sufficient time is allowed, produces uniformity of composition throughout the alloy. Often conditions are not suitable to allow complete interdiffusion between the constituents, and a complex structure results.

Commercial alloys usually contain more than two elements, sometimes intentionally and sometimes unavoidably. Steel, for example, practically always contains, besides iron and carbon, the elements, manganese, silicon, sulphur, and phosphorus. The solidification of pure metal is dendritic in nature, as described in Chap. III. The solidification of the primary crystals in solid solution alloys is also dendritic in nature. The dendrites originally contain the purest solvent metal along the main trunk and branches and the other elements are largely concentrated in the last portion to solidify, which is that portion between the branches, sometimes called "interdendritic." If diffusion in the solid state is complete, all traces of the original dendrites may be removed. In the case of steel, however, the phosphorus atom, in particular, seems to be too large to diffuse readily in the iron space lattice. The phosphorus atoms, having been concentrated during solidification in the portions between the branches of the dendrites, may remain partially segregated, even after transformation in the solid state in the steel and after a considerable amount of mechanical working. Professor A. Sauveur¹

¹ "Crystallization of Iron and its Alloys," *Trans. Am. Soc. Steel Treating*, p. 12, July, 1923.

shows how these segregated structures in steel may persist, even after mechanical working and heat treatment.

Examples are given in Figs. 116 and 117, showing how a cast alloy may consist of two constituents, whereas, after the influence of mechanical working and heating, complete diffusion has taken place, resulting in the elimination of one of the constituents and in the production of a substantially uniform composition in the remaining constituent.



FIG. 116.—Brass containing 35 per cent zinc as cast. $\times 50$. (Bassett.)

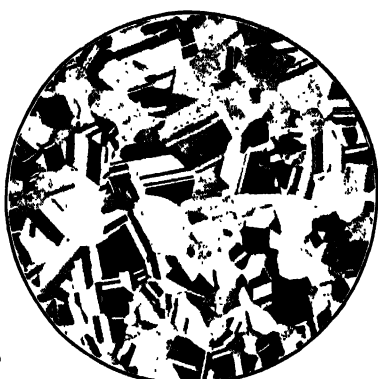


FIG. 117.—Brass containing 35 per cent zinc worked and annealed. $\times 50$. (Bassett.)

Eutectics.—The constituents of eutectics may be any of the primary constituents, namely, pure metals, solid solutions, or intermetallic compounds. Eutectic alloys have a great variety of structures, depending on the nature and proportions of the constituents, as well as on the conditions obtaining during solidification. It is one of the requirements of a eutectic that the constituents form a conglomerate, *i.e.*, that they segregate during freezing. Methods for calculating the amounts of the constituents in eutectics, from the equilibrium diagrams, were discussed in Chap. IX.

Binary eutectics practically never have equal weights or volumes of the two constituents. In some cases the eutectic consists of over 90 per cent of one constituent. In such cases the constituent present in the greatest proportion forms the continuous matrix in which is embedded the other constituent. An example of such a structure is shown in Fig. 118. Here the continuous constituent is aluminum. The alloy is plastic and

relatively soft. The compound, FeAl_3 , is hard and brittle but, because of the relatively small quantity present and its arrangement, it has only a moderate hardening effect on the aluminum.

F. L. Brady¹ classifies the structure of eutectics under four heads, as follows:

1. Globular.
2. Lamellar.
3. Angular.
4. Crystalline.

Perhaps the lamellar structure is the most typical. The constituents solidify in alternate thin plates. Sometimes the



FIG. 118.—Aluminum alloy containing 1.75 per cent iron slowly solidified. $\times 500$. (Dix.)

FIG. 121.—Normal aluminum-silicon eutectic. $\times 500$. (Dix.)

plates are nearly flat, but more often they are irregularly curved. Figure 119 is a micrograph of the lead-tin eutectic, magnified 150 diameters. This shows a typical lamellar structure. The tin is the white and the lead the dark constituent. Close observation will reveal the fact that the tin is the continuous constituent. This alloy is soft and behaves more like tin than lead.

The globular eutectic structure is also very common. Figure 120 shows the globular structure of the copper-silver eutectic. The silver-rich solid solution is the continuous phase and the copper-rich material is in the form of globules.

¹ "The Structure of Eutectics," *J. Inst. Metals*, vol. 28, p. 369, 1922.

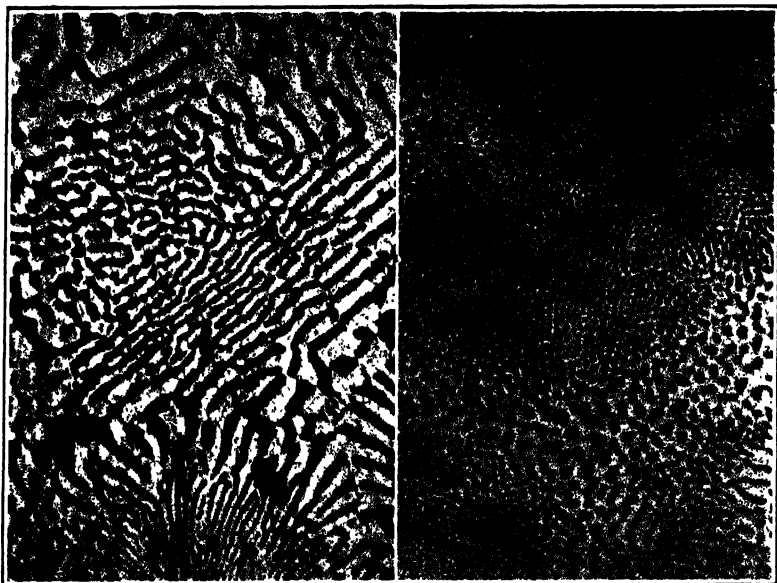


FIG. 119.—Lead-tin eutectic. $\times 150$.
(Brady.)

FIG. 120.—Silver-copper eutectic.
 $\times 300$. (Brady.)

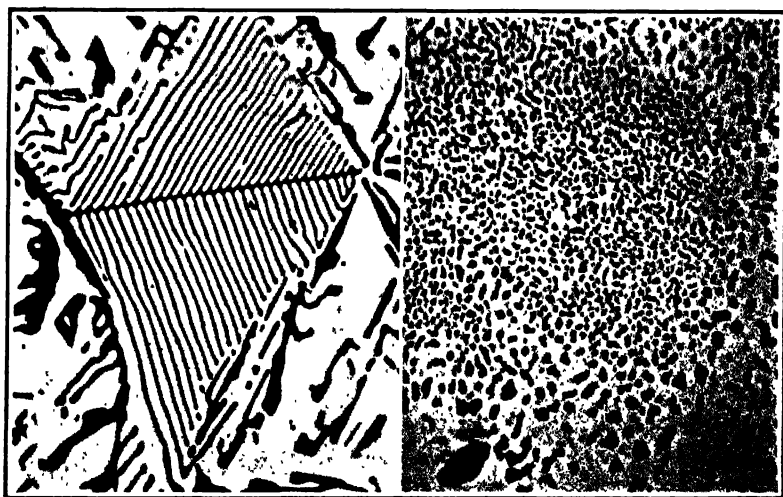


FIG. 122.—Normal aluminum-silicon
eutectic with "angular" structure.
 $\times 500$. (Dix.)

FIG. 123.—Modified aluminum-silicon
eutectic. $\times 500$. (Dix.)

When one of the constituents of a eutectic forms in crystalline particles with some of the geometrical crystal faces developed, Brady refers to the structure as "angular." The "crystalline" eutectics are more typical of rock mixtures than of metallic alloys. The aluminum-silicon eutectic, when formed by sand casting a 10 per cent silicon alloy, is shown in Figs. 121 and 122. This is the eutectic in "normal" aluminum-silicon alloys. This structure would be classed as angular. The structure of the eutectic is changed to globular by the addition of a very small amount (0.02 per cent) of sodium. Not only is the type of structure changed but so also are the proportions of aluminum and silicon in the eutectic, the freezing point, and the degree of dispersion of the silicon.¹ Aluminum-silicon alloys treated with sodium are referred to as "modified." This structure is shown in Fig. 123.

As a result of this change in structure there is a marked increase in tensile strength and ductility.

Properties of Eutectics.—Unless the constituent particles of the eutectic are very small, many of the properties are approximately what would be expected from the proportions and properties of the constituents. Owing to the obstructing effect of each constituent on the grain growth of the other during solidification, eutectics are practically always fine-grained as compared to pure metals and solid solutions similarly cooled. The hardness of a eutectic is, therefore, usually greater than that calculated on the assumption of linear variation. Also, chilling has a greater effect on the hardness of eutectics than on pure metals. Table XIX shows the Shore scleroscope (magnifier hammer) hardness of certain eutectic alloys slowly cooled and chilled.

TABLE XIX (Brady)

Eutectic	Slowly cooled	Quenched
Lead-tin	8	11
Zinc-tin	11	17
Cadmium-lead .	17	23
Zinc-cadmium .	24	37

Portevin² gives the Brinell hardness numbers of certain binary eutectics as shown in Table XX.

¹ Refer Chap. IX, p. 325.

² "The Structure of Eutectics," *J. Inst. Metals*, vol. 29, p. 239, 1923.

TABLE XX

Eutectic	Brinell hardness numbers	
	Slowly cooled	Chill cast
Lead-tin.....	21 32	27.52
Lead-cadmium. . .	13. 72	18.84
Bismuth-tin.....	16. 48	24 04
Lead-antimony. . .	14. 28	20.36
Bismuth-cadmium.	16 76	21.68
Lead-bismuth. . . .	14. 04	14.36
Aluminum-zinc *	74 00	100.40

In order for a eutectic to be plastic, the continuous phase must be plastic. The plasticity of the alloy is greater if the "disperse" (discontinuous) phase is plastic than if it is brittle. In cases where a certain eutectic may have different structures it is found that the globular structure is most conducive to plasticity. When the eutectic is "fine-grained," it may have more capacity for being deformed without rupture than when coarse-grained, but it usually takes a greater load to effect a given permanent deformation.

The normal aluminum-silicon eutectic alloy, with a structure as shown in Fig. 121, has a tensile strength of about 20,000 lb. per square inch and elongation in 2 in. of about 2.5 per cent on a $\frac{1}{2}$ -in. diameter, sand-cast test bar. The modified eutectic, with a structure as shown in Fig. 123, has a tensile strength of 27,500 lb. per square inch and an elongation of 7 per cent.

The Eutectic as a Constituent.—Although the structure of the eutectic is itself complex, it is regarded as a sufficiently definite entity to be classed as a constituent of alloys of which it is only a part.

Eutectic and Excess Constituent.—Alloys in a binary eutectiferous system, other than the eutectic alloy itself or solid solutions which may form in alloys at either end of the series, consist of eutectic and excess constituent. If A and B are the constituents of a binary eutectic, then such alloys, in accordance with their composition, will contain eutectic and excess A or eutectic and excess B.

In these alloys there is a tendency for the eutectic to surround the excess constituent. The excess constituent, of course, freezes out first and is completely solid before any of the eutectic solidifies. The solid eutectic will therefore occupy the same position as the liquid of eutectic composition just prior to solidification. If the quantity of excess constituent is large and the quantity of eutectic is small, the excess constituent will be continuous, even though it appears to be substantially surrounded by a network of eutectic. As the proportion of excess constituent becomes less, and the eutectic greater, a composition is reached where the eutectic surrounds the excess constituent and becomes the continuous constituent. If there is marked difference in physical properties between the eutectic and the excess constituent, there will be a marked difference between the physical properties of the alloys in which the excess constituent is the continuous constituent and those in which the eutectic is the continuous constituent.

The mechanical properties of alloys consisting of eutectic and excess constituent vary in an approximately linear manner with change in quantities of eutectic and excess constituent, if both are plastic.

The actual quantity of eutectic in an alloy may be more or less than the amount calculated from the equilibrium diagram. The same conditions which cause the formation of two constituents in certain solid alloys, when the equilibrium diagram demands one, cause the formation of more eutectic and less excess substance than the equilibrium amounts. An aluminum alloy containing 4 per cent of copper may be considered as an example. Under equilibrium conditions, aluminum will hold about 5 per cent of copper in solid solution at the eutectic temperature, 542°C . The constituents of the eutectic are this saturated solid solution and the compound, CuAl_2 . Under ordinary conditions of solidification an alloy containing 4 per cent of copper does not form a homogeneous solid solution. The first crystals to freeze out contain less than 4 per cent of copper and, by the time the solidification process is complete, the concentration of copper in the last traces of liquid has reached the eutectic composition. Castings of this alloy therefore contain some of the eutectic, although under conditions of equilibrium eutectic would not appear until the copper content exceeded 5 per cent.

When the eutectic consists largely of one constituent and the composition of the alloy is such that there is an excess of this constituent, it often happens that the principal constituent of the eutectic will crystallize, in part, on the excess material. In such cases it is not possible to distinguish that part of the eutectic from the excess constituent. Alloys of copper and cuprous oxide sometimes show less eutectic than the calculated amount because some of the eutectic copper crystallizes on the excess copper.

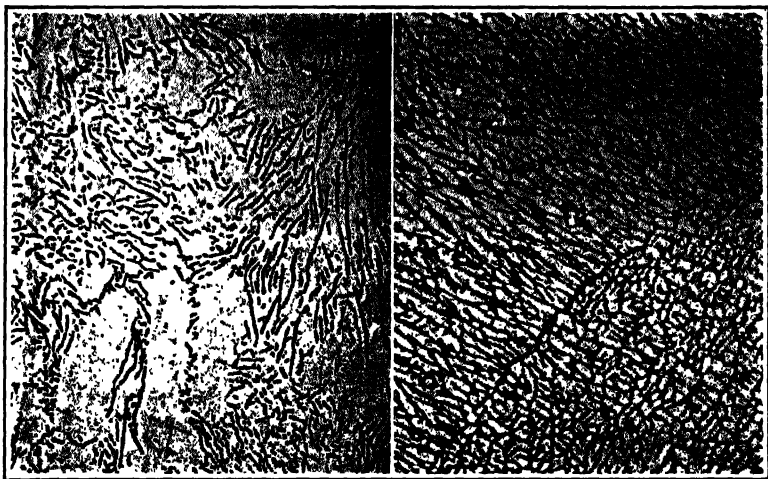


FIG. 124.—Aluminum- FeAl_3 eutectic plus excess aluminum slowly solidified. $\times 100$. (Dix.)

FIG. 125.—Aluminum- FeAl_3 eutectic plus excess aluminum rapidly solidified. $\times 100$. (Dix.)

Effect of Rate of Solidification on Cast Alloys.—Figure 124 is a micrograph of a slowly cooled aluminum-iron alloy containing 1.75 per cent iron. Figure 125 is a micrograph at the same magnification of the same alloy rapidly solidified. The white areas are in each case excess aluminum and the dark areas represent the aluminum- FeAl_3 eutectic. Figure 126 is a micrograph of the same specimen as Fig. 125, but magnified ten times as much. Howe was in favor of calling each island or near island of excess substance, with a portion of the surrounding material, a "cell." Many "cell" structures originate from the dendritic crystal growth of the excess substance. The real grains are very large as compared to the cells. The grains are the primary dendrites and the cells the many fillings between trunk and branches.

Figure 126 shows part of one grain, but several cells. In Fig. 125 there are parts of two grains shown, but many cells. In an alloy of this sort the rapid solidification has not only greatly



FIG. 126.—Aluminum-FeAl eutectic plus excess aluminum rapidly solidified. $\times 1,000$. (Dix.)

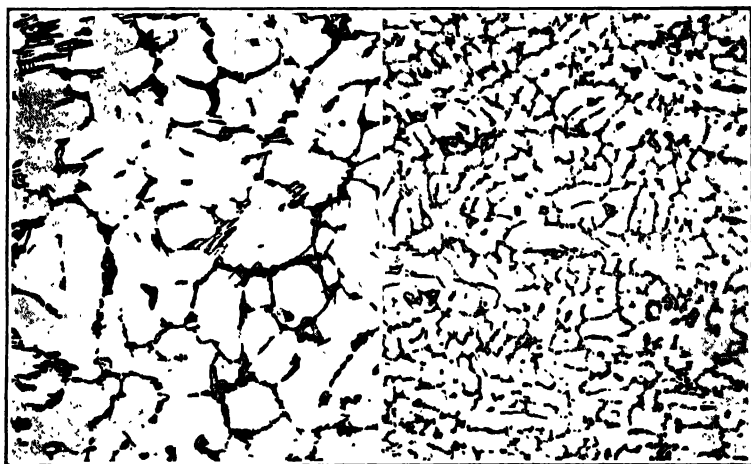


FIG. 127.—Aluminum piston alloy, sand-cast. $\times 100$. (Dix.)

FIG. 128.—Aluminum piston alloy, chill-cast. $\times 100$. (Dix.)

reduced the cell size, but the constituents of the eutectic have been even more refined, as would be expected from considerations discussed above. The cell size in Figs. 124 ($\times 100$) and

126 ($\times 1,000$) is roughly the same on the micrographs but the eutectic in Fig. 126 appears much the finer "grained."

Figure 127 is a sand-cast aluminum alloy containing about 10 per cent copper, 1.25 per cent iron, and 0.25 per cent magnesium. Figure 128 is a micrograph at the same magnification of this alloy cast in an iron mold. The light-colored constituent is the excess aluminum (containing a little copper in solid solution), and the dark constituent is essentially the aluminum CuAl_2 eutectic. The "chilling" effect of the iron mold has caused a marked reduction in cell size and a refinement of the eutectic.

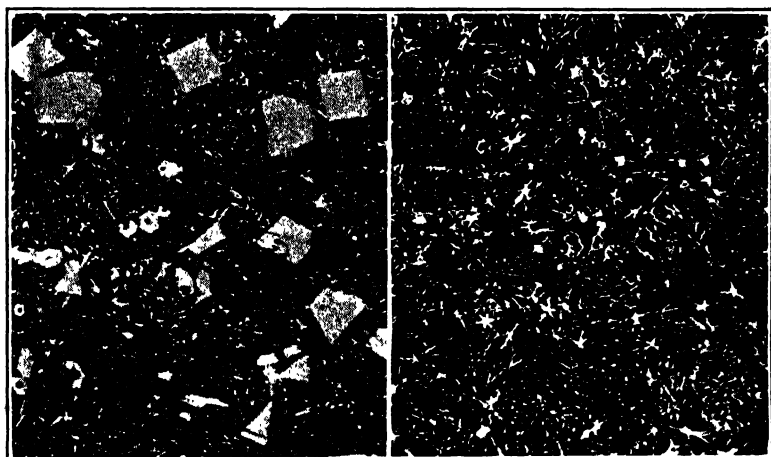


FIG. 129.—Babbitt metal slowly solidified. $\times 100$.

FIG. 130.—Babbitt metal rapidly solidified. $\times 100$.

The Brinell hardness number of the sand-cast alloy is 80 and that of the chill-cast specimen 100. This is an aluminum piston alloy and Fig. 128 is a typical structure of a commercial piston.

Figure 129 is a micrograph of babbitt solidified at a moderate rate. The babbitt contains about 84 per cent tin, 7 per cent copper, and 9 per cent antimony. Figure 130 is a micrograph of the same alloy, which has been solidified more rapidly. Figure 130 represents a good structure for a commercial bearing. The white constituents are compounds of tin with antimony and with copper, while the dark area, or matrix, is a tin-rich ternary eutectic. The Brinell hardness number of the slowly solidified babbitt was 31.2 and that of the more rapidly solidified one, 40.8.

Figure 131 is a micrograph of a tin bronze containing 87.7 per cent copper, 10.7 per cent tin, 0.27 per cent lead, and 0.23 per cent aluminum. The dendrites consist of the Alpha solid solution of tin in copper, the shading being due to the coring or variation in tin content. Between the dendrites are occasional small angular areas, scarcely visible at this magnification, of the Delta or "eutectoid" constituent. This specimen was cut from a chilled gear blank from a portion remote from the "chill." The tensile strength was 27,000 lb. per square inch and the elongation 5 per cent. Figure 132 shows a specimen taken from the same gear blank at a point near the chill. A refinement and

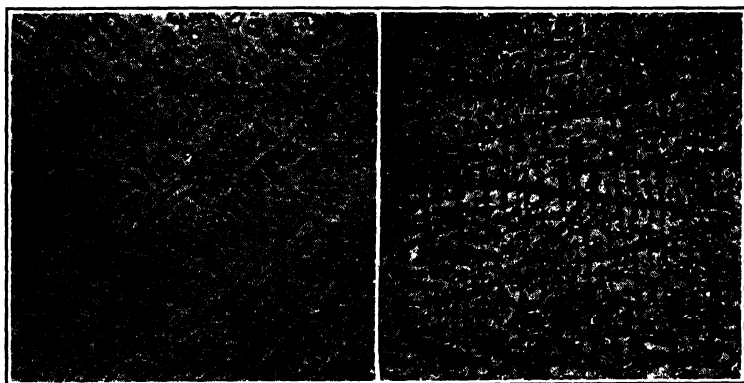


FIG. 131.—Gear bronze solidified slowly. $\times 50$.

FIG. 132.—Gear bronze rapidly solidified. $\times 50$.

a greater perfection of the dendritic structure are apparent. The tensile strength of this specimen was 45,000 lb. per square inch and the elongation 20 per cent.

Structures of Alloys Having Incomplete Liquid Solubility.—There are few important metallic mixtures, or "alloys," if that term may be properly applied, which are formed by the solidification of liquid mixtures. About the only ones of commercial importance are those formed by the addition of lead to copper, bronze, or brass.

The constitution of the copper-lead system has been described in Chap. IX. At temperatures above the melting point of copper, this system consists of two liquid phases: copper containing a small amount of lead in solution, and lead containing a small amount of copper in solution. If unagitated, these phases

will separate into two layers, the copper-rich layer floating on the lead-rich layer. Undisturbed cooling would permit the two layers to solidify separately. If, however, the liquid mixture is stirred vigorously and solidified quickly, as by casting in a chill mold, a more or less intimate mixture or "alloy" is obtained. Such alloys, containing up to 50 per cent by weight of lead, are used for certain classes of heavy-duty bearings.

The copper solidifies first, in the usual dendritic manner, rejecting practically all of the lead as it cools to the freezing point, since the two metals are insoluble in the solid state. When the mixture contains 50 per cent of lead by weight, it contains only about 45 per cent by volume and, if the alloy is properly made, the copper is the continuous constituent, the lead occurring as disconnected globules. Consequently, the alloy has more nearly the properties of copper than of lead. Its hardness and plasticity are intermediate between those of copper and lead. The value of the material as a bearing metal depends on its plasticity, and on the lubricating or antifrictional quality of the lead.

Lead is added to many bronzes to improve their bearing qualities for certain kinds of service. The less the amount of lead added, the more easily can it be obtained in a uniformly dispersed and finely divided condition. It is also the general practice to add about 3 per cent of lead to brass used for automatic screw machine work, or whenever machineability is the primary requisite. The lead causes the chips to break more quickly and also probably has some value as a lubricant on the tool.

It has been found that the addition of certain substances, notably lead sulphide, to the copper-lead mixture greatly assists in retaining a good dispersion of the lead in the copper. Some such addition is nearly always used in the commercial preparation of the alloy. It is not necessary in the case of brass or bronze.

On the other hand, it appears that the presence of even a trace of aluminum (less than 0.1 per cent) ruins brasses which contain lead, apparently by causing separation of the lead in an unfavorable manner. If lead is absent, brass is improved by small amounts of aluminum.

Effect of Heat on Solid Alloys.—The final structure and properties of an alloy depend, sometimes to an important extent, on its thermal treatment in the solid state. Such treatment

may consist merely of the natural cooling of the alloy from the freezing point to ordinary temperatures, or may involve definite "heat treatment," in which the temperature and time factors are more exactly controlled. The effect depends on the same fundamental principles, whether the thermal treatment is natural or directed, but may be considered more simply from the viewpoint of the artificial heat treatments.

Homogenizing.—Reference has been made elsewhere to the fact that cast alloys which are made up of cored dendrites of a single solid solution, such as Alpha brass, can be rendered homogeneous by sufficiently prolonged heating at temperatures below the melting point. An entirely similar effect can be produced in many alloys containing two or more constituents. A cast brass containing 30 per cent of zinc, for example, contains two constituents, the Alpha and Beta solid solutions, but can be converted, by sufficient annealing at about 700° C., to homogeneous Alpha solid solution.

The possibility of marked change in this way exists only when one constituent of the alloy is a solid solution of considerable concentration. This constituent is cored in the cast alloy, and the heating process produces homogeneity. Some or all of the excess constituent may go into solution. Since this process depends on diffusion, the temperature must be sufficiently high to allow diffusion to take place. This must, in general, be above the recrystallization temperature of the solid solution.

The effect of a homogenizing treatment on the properties of an alloy must be considered for each case from the standpoint of the structures before and after treatment. In the case of the 70:30 brass, the change in properties is not very marked, because the properties of the two constituents involved, the Alpha and Beta solutions, are not radically different. More striking effects are obtained by the heat treatment of certain copper-tin alloys, or bronzes.

Under equilibrium conditions, copper can hold in solid solution, at room temperature, about 13 per cent of tin. An alloy containing 10 per cent of tin does not, as cast, consist entirely of this Alpha solid solution. Because of the coring effect during solidification, the tin is concentrated between the Alpha dendrites, and a second constituent, the Beta solid solution, is formed. This constituent becomes unstable on cooling at 525° C. and breaks up into a eutectoid mixture of Alpha solution and the Delta

phase, which is believed to be the compound, Cu_4Sn . The cast alloy at room temperature is thus made up of cored Alpha dendrites with angular interdendritic areas of the eutectoid constituent. This alloy is the best known of the bronzes. It is commonly called gun metal, from its use in the construction of ordnance before the advent of iron and steel for this work. With the addition of 2 per cent of zinc, it is called Admiralty bronze, or 88:10:2, and is extensively used for castings for marine work, for bearings, and for gears. When used for bearings or gears, a little phosphorus may be added to the alloy, in which case it may be called phosphor-bronze. When properly made and cast in sand, it has a tensile strength of about 35,000 lb. per square inch and an elongation of about 18 per cent.

The Alpha copper-tin solution is somewhat stronger than copper and more ductile, as measured by per cent elongation. The Delta constituent, and, in fact, the eutectoid as a whole, is extremely hard and strong, but very brittle. Its presence adds elasticity to the alloy, but reduces its plasticity and ductility. When the alloy is used as a bearing metal, the hard eutectoid areas stand out in slight relief and take the wear, allowing the lubricant to fill the depressions in the matrix.

On reheating this alloy to about 700°C. , the eutectoid areas are reconverted to Beta solid solution and, on holding at this temperature, diffusion takes place, until, finally, homogeneous Alpha solution is obtained. After cooling to room temperature, the alloy is found to be stronger and the elongation may be doubled. The increase in strength is due to the enrichment of the Alpha constituent and the elimination of brittleness caused by the eutectoid. Because of the removal of the eutectoid, however, the alloy is less useful as a bearing metal. The heat treatment is seldom practiced commercially.

Although the effects of a homogenizing treatment depend, in each case, on the specific structural changes involved, it may be stated, as a general rule, that the plasticity and ductility are increased markedly. The strength and hardness may also be increased, but usually to a less marked extent. The possibility of such a generalization is based on the fact that the first solid solution of an alloy system is usually the most ductile constituent, the next constituent formed, whether compound or solid solution, being harder and more brittle. This second constituent also has a tendency to form in the grain boundaries of the alloy, as a sort

of network which is more or less continuous, depending on the quantity of the second constituent present.

Spheroidizing and Particle Growth.—In an alloy containing disconnected particles of a constituent possessing even a slight solubility in the matrix, these particles tend to increase in size and become rounded when the alloy is heated at the proper temperatures. The most familiar example of this action is found in the eutectoid constituent, pearlite, of steels. Prolonged heating just below A_1 (725°C.) causes the thin curved lamellæ or plates of cementite to become rounded in shape until they are finally approximately spherical. In this case the change in shape is the most striking result, and the process is called *spheroidizing*.

When the particles are initially of almost spherical shape, like the cementite in troostite or sorbite, the same sort of heat treatment produces particle growth.

Both the spheroidizing and the growth are results of the tendency toward the reduction of the ratio of surface to volume. The causes and mechanism of the process are discussed in other chapters.

This type of structural change is the general rule rather than the exception, and has been observed in the case of many constituents in many alloys. Conditions favoring the change are: (1) small size of dispersed particles; (2) departure from spherical shape; (3) solubility in matrix. The change appears to be possible when the solubility is so slight as to be practically unmeasurable. The thermal treatment favoring the change is prolonged exposure at the highest possible temperatures below the point of incipient fusion, or the point at which the constituent to be spheroidized passes completely into solid solution.

The changes affect only that part of the constituent which is not in solution. Consider, for example, a steel containing 1.3 per cent carbon, in the form of cementite plates. Prolonged heating at about 700°C. would cause the spheroidizing of all of the cementite, with the exception of the small amount soluble at that temperature, about 0.05 to 0.10 per cent carbon (provided, of course, that the composition of the steel was not such as to cause graphitization). If the heating is carried out above A_1 , say, at 750°C. , about 0.95 per cent carbon will be in solution in the austenite, and it is only the remaining undissolved cementite which will be spheroidized.

The effects of spheroidizing and particle growth on physical properties can, in general, be predicted. The particles concerned are usually harder and less plastic than the matrix in which they are embedded. Their presence therefore increases the hardness and reduces the plasticity of the alloy. The growth and spheroidizing of hard particles will decrease these effects, and therefore render the alloy softer and more plastic. The tensile strength will be reduced unless it was initially abnormally low because of the brittleness of the alloy. In such a case the spheroidizing process might simultaneously decrease the hardness and increase the strength.

Heat Treatment Effects Due to Phase Changes.—When the constitution of a solid alloy is different at different temperatures, its final structure is obviously influenced to a large extent by its thermal treatment. In general, very slow cooling allows the attainment of the constitution stable at room temperature. Cooling rapidly, as by quenching, from a high temperature may cause the retention of the structure existing at that temperature. It is often impossible to do this, however, even by the most rapid cooling, in which cases there is a more or less complete change toward the equilibrium stable at lower temperatures.

Certain brasses and bronzes are examples of this class of alloys. A brass containing 65 per cent copper and 35 per cent zinc is 100 per cent Alpha at room temperature, but at 850° C. is approximately half Alpha and half Beta. Quenching this brass from 850° C. preserves the Alpha plus Beta structure at room temperature, whereas slow cooling produces only the Alpha constituent. The Alpha plus Beta structure is harder and less plastic than the Alpha, owing to the fact that Beta brass is harder and less plastic than Alpha.

The solubility of copper in aluminum in the solid state varies so much with temperature that the properties of aluminum-copper alloys can be changed by heat treatment. This case will be discussed later in connection with the alloys in the worked condition.

Commercial Heat Treatments.—The importance of heat treatment in determining the structure and properties of an alloy is indicated by the extent to which such heat treatment is practiced. The heat treatments commonly applied are few in number, and the most important are covered by the following list:

1. Annealing of cold-worked metals and alloys to remove or reduce work hardness. This has been fully discussed for pure metals and solid solutions, and is not essentially different for aggregates.

2. Annealing of worked or cast alloys to remove internal stresses. Although the removal of internal stresses may improve the properties of the article as a whole, there is usually no visible structural change or important change in the properties of the material.

3. Annealing of steel castings. The primary object is grain refinement, but there is also some improvement due to homogenization. The refinement of grain results from the recrystallization on passing through A3, or the line *GS* of the iron-cementite diagram.

4. Annealing of white iron castings for the production of malleable castings, the structural change being graphitization. This is discussed elsewhere rather fully.

5. Refining of the grain of worked steel by heating above the line *GSK* of the iron-cementite diagram. The temperatures employed are ordinarily higher than for hardening.

6. Hardening of steel by cooling rapidly from just above *GSK*. This is by far the most important heat-treating operation practiced. The mechanism of the process is discussed very fully in Chap. XII, where the heat treatment of high-speed steel, a special case, is also considered.

7. Tempering of hardened steel by reheating to temperatures below A1. The mechanism of this process is likewise discussed fully in Chap. XII.

8. The heat treatment of certain light aluminum alloys, such as duralumin, to increase strength and hardness. The fundamental mechanism of this operation is discussed subsequently in this chapter.

9. The properties of aluminum bronze (copper 90 per cent, aluminum 10 per cent) can be markedly altered by heat treatment, and this is practiced to a limited extent commercially.

Deformation of Aggregate Containing Brittle Constituent.—It will be recalled that a cast bronze of the 88:10:2 variety is made up of dendrites of the Alpha solid solution of tin in copper, with occasional areas of the hard and brittle eutectoid constituent between the grains. Rawdon has studied the behavior of these

constituents when a test bar of the alloy is broken in tension.¹ It was found that in test bars of high strength and elongation, plastic deformation took place in the Alpha solution, while the bodies of eutectoid were broken into fragments which were then displaced with respect to each other by the deforming process. In test bars which, because of included oxide films, gave very low strength and elongation, the eutectoid areas were found to be intact after rupture of the test bar.

The conditions observed in this bronze are typical of the deformation of aggregates. Plastic deformation can take place only in the plastic constituents, which, as a rule, are pure metals or solid solutions. Inclusions of brittle constituents, such as intermetallic compounds, metalloids, oxides, slag, etc., tend to be broken up. This tendency is greater the more extended the form and the larger the size of the brittle inclusions. With a given shape and size of brittle particles, an alloy will withstand a certain limited amount of permanent deformation before the brittle constituent begins to break up, provided the brittle constituent does not form a substantially complete network. Further deformation will cause fragmentation of the brittle constituent. The amount of deformation possible before this occurs is greater as the brittle particles become smaller and as their shape approaches that of spheres. An alloy made up of small, hard, brittle spheres embedded in a plastic matrix could be subjected to an almost unlimited amount of deformation without producing fracture in the brittle constituent.

Hot Working Develops Continuity of Plastic Constituent.—

It is often possible, though difficult, to hot work alloys which, as cast, contain practically complete brittle networks around the grains. Cast steels containing as high as 2.65 per cent of carbon have been successfully forged. The initial working or "breaking down" of such alloys must be done very gently and carefully but, as the working proceeds, the plasticity of the aggregate increases. Many alloys which are very tender as cast can be worked drastically after breaking down. This is due largely to the breaking up of the brittle constituents, and the flow of the plastic constituent around the fragments. Mechanical working thus creates or perfects the continuity of the plastic constituent.

¹ "Standard Test Specimen of Zinc Bronze," *Trans. Am. Inst. Metals*, vol. 9, 1915.

Cold working breaks up brittle constituents even more effectively than hot working involving the same amount of total deformation, and a certain amount of healing or internal welding is possible in metals below their recrystallization temperatures. Cold working followed by annealing may, therefore, be considered as a means of developing plasticity. The amount of cold work that can be carried out on a somewhat brittle aggregate is quite limited, however, as is also the ability of the plastic constituent to flow around the fragments of the brittle constituent and heal together. Cold working cannot, therefore, in general, be considered as a practical means of developing plasticity.

Deformation of Aggregates in General.—The discussion immediately preceding has referred particularly to aggregates in which one constituent is decidedly plastic while one or more other constituents are present of a decidedly brittle nature. When two or more plastic constituents are present, deformation takes place in each, more or less in proportion to its softness. Lead and tin, for example, are both plastic, and hence the lead-tin eutectic can be rolled or extruded with ease. Both constituents deform easily. Any sort of mixture of lead and tin would be plastic. Ferrite and pearlite, in steel, have quite different degrees of plasticity and softness, and, consequently in the working of a ferrite-pearlite aggregate the ferrite, being more plastic, is deformed more than the pearlite.

The pearlite itself is a complex, consisting of ferrite (continuous phase) and cementite. Cementite is devoid of plasticity. Mechanical working of pearlite deforms only the ferrite; the cementite is either broken and moved with the ferrite or remains intact, while the ferrite is deformed. Any considerable working of lamellar pearlite breaks the plates of cementite and separates them from one another, and thus produces a mechanical refining effect on the cementite particle size. Reheating cold-worked lamellar pearlite produces globular cementite more readily than in material not cold worked.

Cold Working of Aggregates.—The effect of brittle hard constituents in an aggregate is to force nearly all of the deformation in the plastic constituents, which, in turn, hardens the aggregate more than the same amount of total deformation would harden the plastic constituent by itself. For example, a given amount of cold work hardens copper containing cuprous oxide more than it would pure copper.

Recrystallization and Grain Growth in Aggregates.—In a cold-worked aggregate, recrystallization and grain growth, as ordinarily understood, take place only in the continuous constituent. Disconnected particles may grow slowly at suitable temperatures, but this action, described above, is not ordinarily called grain growth. For a given amount of deformation, the recrystallization temperature of an aggregate is lower than that of the continuous constituent alone, since the hardening effect is greater. The extent of the grain growth is limited, however, by the obstructing action of the other constituents of the aggregate, unless these should happen to be present in such quantity and form as to cause germination.

Refining Effect of Mechanical Work.—Mechanical working changes the orientation of the various fragments between slip



FIG. 133. Muntz metal as cast. $\times 50$. (Bassett.)

planes in the original grains, the change being slight for mild deformations and becoming greater as the amount of deformation increases. If the work is done hot, some of the differently oriented grain fragments spontaneously form new grains smaller than those in the cast ingot. The general effect is, therefore, one of grain refinement. If the working is done cold, the grain fragments produced by the deformation remain substantially unchanged, unless the metal is heated to or above its recrystallization temperature. By such heating, grain growth among the fragments takes place, the normal result being a larger grain size the higher the temperature and the longer the time of heating.

The resulting structure is similar to that of a hot-worked metal. The larger grain size of the cast metal is due to the fact that large grains are toward more perfect equilibrium and the high temperature of the metal during solidification permits approach toward equilibrium. Mechanical working (if the deformation is sufficient) produces grain fragments much smaller than the equi-

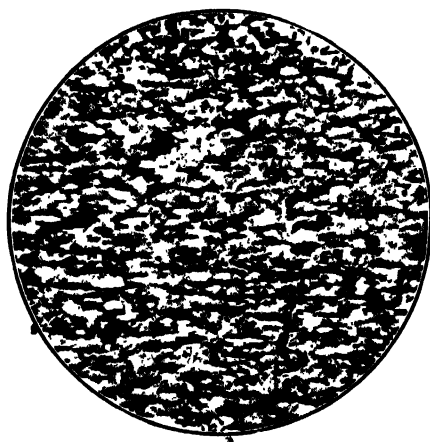


FIG. 134.—Muntz metal hot rolled. $\times 50$. (Bassett.)

librium grain size for temperatures well below the melting point. Growth of the fragments therefore takes place on heating, but the grain size attained by growth in the solid state is normally smaller than that of cast metal (see Figs. 116 and 117). The grain size of a hot-worked metal is generally smaller the lower the finishing temperature.

Figure 133 is a micrograph of cast Muntz metal (60 per cent copper and 40 per cent zinc). Figure 134 is the same material after hot working. This alloy consists, structurally, of the Alpha constituent (white) and Beta (black). It will be noted that the size of the units of Alpha and Beta has been greatly reduced by the hot working.

Figure 135 is a micrograph of the Muntz metal hot worked and then cold worked. The particles of both constituents are elongated in the direction of extension of the piece as a whole.

In the working of steel, a peculiar condition obtains because in the hot-working range most steels are substantially solid solutions (austenite) and are aggregates only after slow or moderate cooling below the critical range. Figure 136 is a

micrograph of cast medium-carbon steel. The ferrite network marks the old austenite grain boundaries. Figure 137 is a medium-carbon steel hot worked and finished in the austenitic

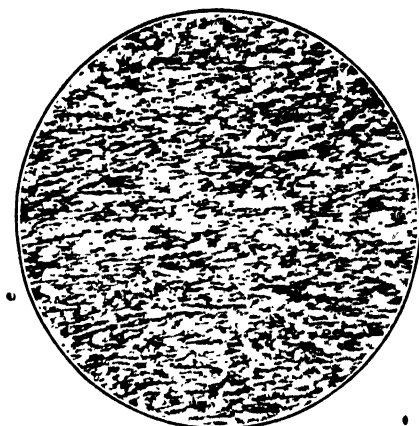


FIG. 135.—Muntz metal hot rolled and then cold rolled. $\times 50$. (Bassett.)

range. The ferrite network which marks the old austenite grain boundaries shows how hot mechanical working refines the

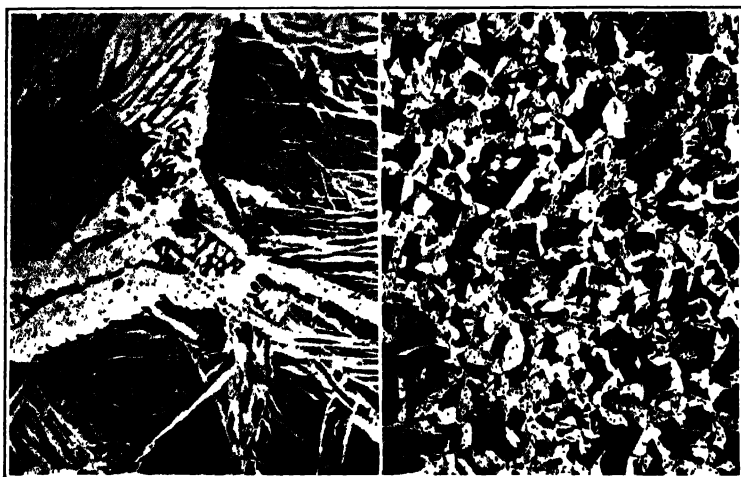


FIG. 136.—Medium-carbon steel as cast. $\times 100$. (R. R. Studler.) FIG. 137.—Medium-carbon steel hot worked. $\times 100$. (Carter.)

austenite grain. Figure 138 is a medium-carbon steel hot worked and finished in the austenite range, cooled to room temperature, and then cold worked.

Fiber.—Mechanical working causes the constituents of an aggregate to be extended in the direction of working and to be arranged to some extent in lines or bands in this direction. It is only too common to find bands of cementite particles in tool steels, formed by the extension of segregated carbide networks by working. In milder steels, ferrite bands are commonly observed, often higher in phosphorus than the steel as a whole. These are sometimes referred to as “ghosts.” Slag and non-metallic inclusions, in general, tend to become arranged in lines parallel to the direction in which the piece has been extended.

This arrangement of the constituents of an alloy into parallel fibers tends to improve the quality of the material when subjected to stresses acting in the direction of working. The properties in a transverse direction are apt to be quite inferior. This is most clearly shown in rods or bars. It must be remembered, in dealing with sheet, that, as a rule, the metal has been extended in all directions parallel to the surface of the sheet. The expression “across the grain” or “transverse,” used in connection with sheet, generally refers only to the direction of finishing. The extent of the difference that may sometimes exist between longitudinal and transverse properties is illustrated by the fact that notched-bar impact tests on heat-treated alloy steels, such as are used for many highly stressed automobile parts, have shown values as low as 2 ft.-lb. on specimens broken so that the fracture is parallel with the “grain,” while specimens of the same material broken across the “grain” showed values around 40 ft.-lb.

Gamma Iron.—There are two modifications of iron, Gamma and Alpha, which play an important rôle in the structure and properties of iron and steel products. Pure Gamma iron is not retained as such at room temperature by any known treatment, so its room temperature properties are not known. On testing iron at progressively higher temperatures, it is found that Alpha iron just below 900° C. has about 25 per cent less tensile strength than Gamma iron just above 900° C. Gamma iron, when there is dissolved in it considerable carbon and manganese or carbon and nickel, can be preserved at room temperature. Figure 139 is the structure of commercial manganese steel in which the Gamma iron has been preserved at room temperature by quenching. The structure is essentially the polyhedral one characteristic of pure metals and solid solutions. The tensile strength of this austenitic manganese steel is about 140,000 lb. per square

inch and the elongation about 50 per cent in 2 in. The reduction of area at fracture is only slightly greater than at other points on the test specimen. That the carbon (1.0 to 1.5 per cent) only contributes moderately to these properties is indicated by results reported by Strauss.¹ A steel containing only 0.05

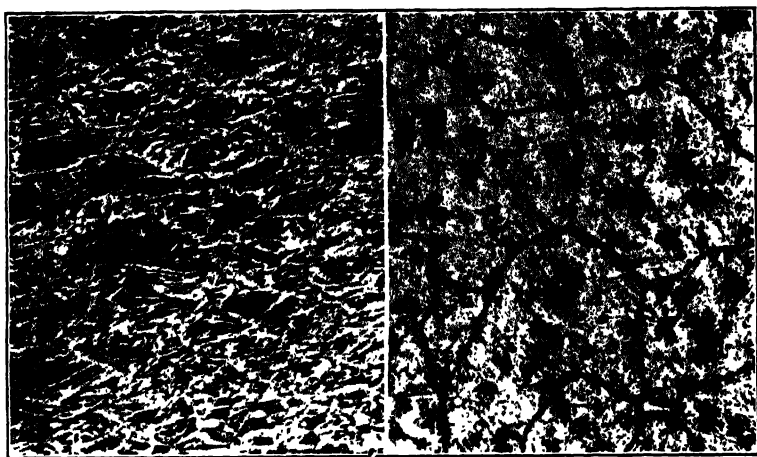


FIG. 138.—Medium-carbon steel hot worked and then cold worked. $\times 100$. (Carter.)

FIG. 139.—Austenitic manganese steel. $\times 100$. (R. R. Studler.)

per cent carbon and 16.00 per cent manganese, quenched from the Gamma iron range, had a tensile strength of 119,000 lb. per square inch and an elongation of 40 per cent.

Alpha Iron.—Alpha iron, either pure or having dissolved in it other elements, such as nickel, manganese, silicon, etc., is referred to as “ferrite.” The origin of ferrite is nearly always from the transformation of austenite. The size of the austenite grains affects the size of the ferrite grains. The influence of an allotrope on the grain size of another allotrope into which it transforms is called “inheritance.”

The most usual occurrence of nearly pure ferrite is in worked products such as wrought iron, ingot iron, and very low-carbon steel. The grain size is usually small as compared to that of cast specimens. Such a structure is shown in Fig. 140. The properties of nearly pure iron with moderate grain size are given in Table VI, p. 152. The ferrite of commercial alloys is hardened by the other elements in solid solution, the most important of

¹ *Trans. Am. Soc. Steel Treating*, Dec., 1923.

which are silicon and phosphorus. The specific effects of these elements are known and can be allowed for. Assuming that these effects are additive, the mechanical properties of the ferrite constituent of steel, malleable cast iron, and gray cast iron have been estimated and the results are given in Table XXI.

TABLE XXI.—MECHANICAL PROPERTIES OF COMMERCIAL FERRITE

Material in which found	Impurities allowed for		Elastic limit, pounds per square inch	Tensile strength, pounds per square inch	Elongation, per cent	Red. of area, per cent	Brinell hardness
	P	Si					
Pure iron.....			18,000	38,000	51	84	70
Steel	0.05	0.25	21,000	45,000	50	82	80
Malleable cast iron..	0.15	0.85	29,000	60,000	48	78	100
Gray cast iron	0.30	2.00	40,000	85,000	43	66	130

Structure of Hypo-eutectoid Steels.—The structure of the iron-carbon alloys will first be considered with respect to the worked

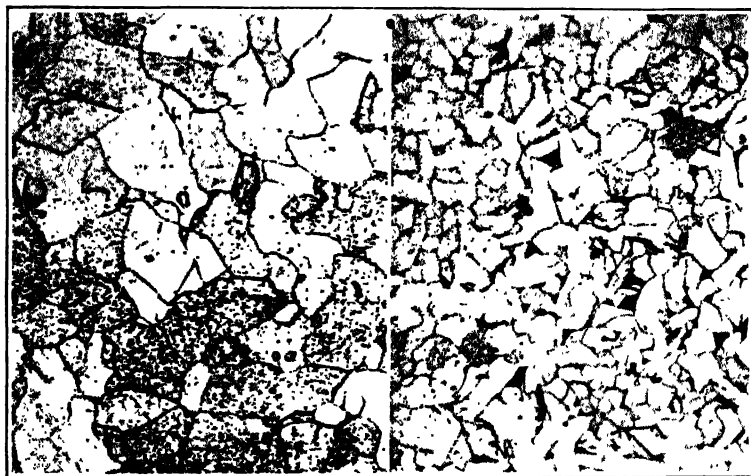


FIG. 140.—Normalized steel, 0.04 per cent carbon. $\times 100$. (*Metallurgical Laboratory, Univ. of Michigan.*)

FIG. 141.—Normalized steel, 0.11 per cent carbon. $\times 100$. (*Metallurgical Laboratory, Univ. of Michigan.*)

steels air cooled from a temperature above the upper critical temperature. A steel so cooled is said to be *normalized* and the heat treatment is referred to as a *normalizing treatment*.

Figure 141 shows the structure of a steel containing 0.11 per cent carbon; Fig. 142, 0.25 per cent carbon; Fig. 143, 0.45 per

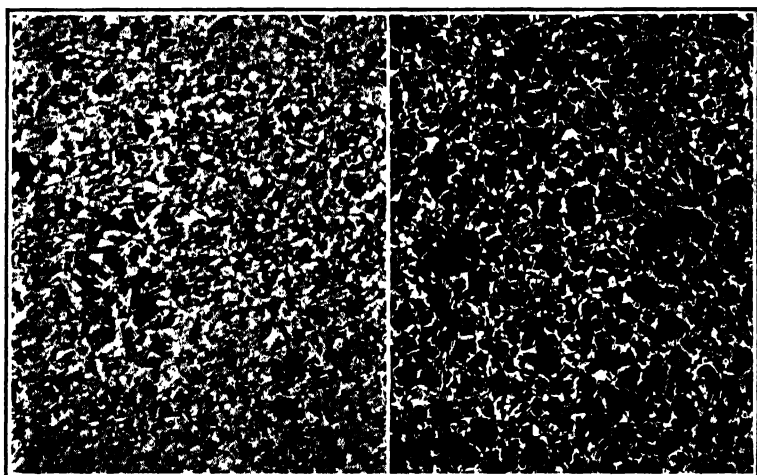


FIG. 142.—Normalized steel, 0.30 per cent carbon. $\times 100$. (Carter.)

FIG. 143.—Normalized steel, 0.55 per cent carbon. $\times 100$. (*Metallurgical Laboratory, Univ. of Michigan.*)

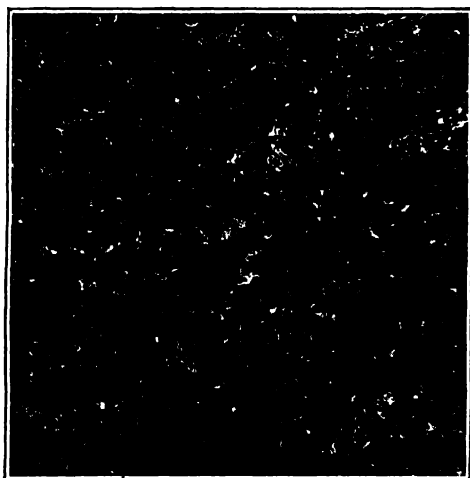


FIG. 144.—Normalized steel, 0.82 per cent carbon. $\times 100$. (*Metallurgical Laboratory, Univ. of Michigan.*)

cent carbon; and Fig. 144, 0.85 per cent carbon, all micrographs being at a magnification of 100 diameters. The light-colored constituent is ferrite and the dark one is pearlite. At this low

magnification the true structure of the pearlite is not revealed. In normalized steels the pearlite is usually lamellar. This structure is shown in Fig. 145 at 250 diameters, Fig. 146 at 500 diam-



FIG. 145.—Lamellar pearlite. $\times 250$. (*Homerberg.*)

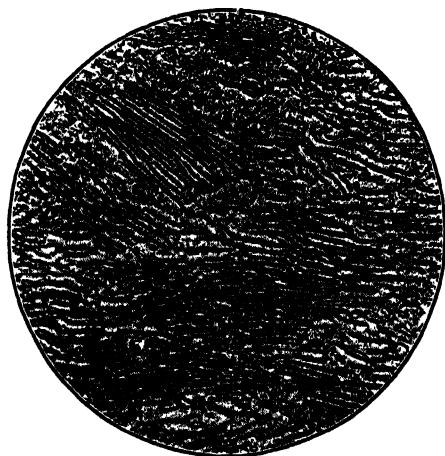


FIG. 146.—Lamellar pearlite. $\times 500$. (*Homerberg.*)

eters, and Fig. 147 at 1,000 diameters. It will be noted that the amount of pearlite increases from zero to 100 per cent as the carbon increases from about 0.05 to about 0.85 per cent. In the commercial steels, always containing some silicon, man-

ganese, phosphorus, and sulphur, the eutectoid point is near 0.85 per cent carbon.

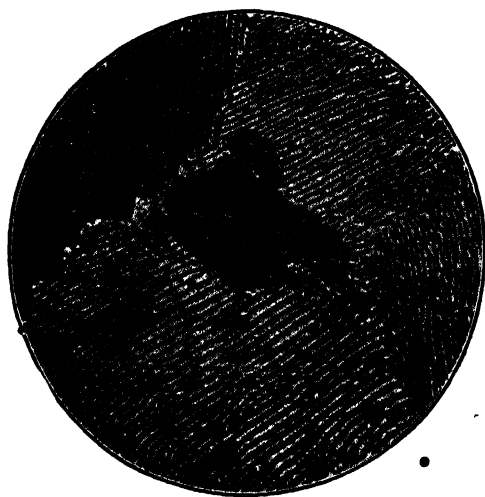


FIG. 147.—Lamellar pearlite. $\times 1,000$. (Walp, S. K. F. Research Laboratories.)

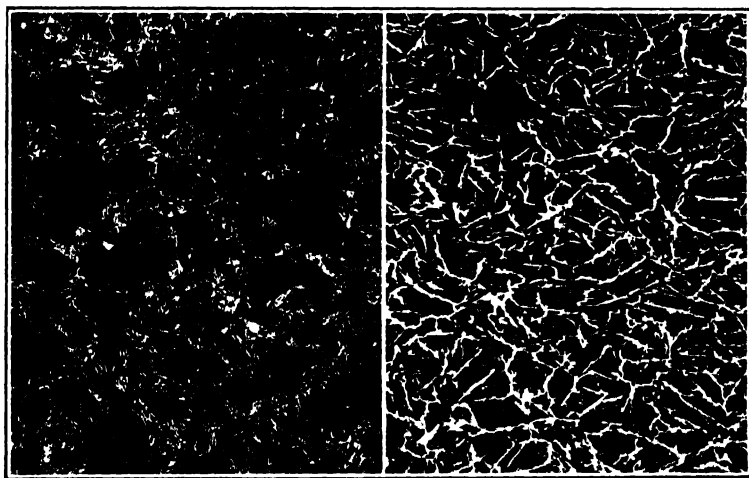


FIG. 148.—Normalized steel, 1.14 per cent carbon. $\times 100$. (Metallurgical Laboratory, Univ. of Michigan.)

FIG. 149.—Normalized steel, 1.65 per cent carbon. $\times 100$. (Metallurgical Laboratory, Univ. of Michigan.)

Structure of Hyper-eutectoid Steels.—As the carbon content increases above 0.85 per cent, the constituents are free cementite

and pearlite. Steels showing, in the normalized condition, free or excess ferrite are called hypo-eutectoid and steels showing free or excess cementite are referred to as hyper-eutectoid. Figure 148 is a micrograph magnified 100 diameters of a steel containing 1.14 per cent carbon. A thin network of cementite at the old austenite grain boundaries can be seen. Figure 149 shows how the cementite increases when the carbon content is increased to 1.65 per cent. The structural change in hyper-eutectoid steels is not so marked for a given change in carbon content as in hypo-eutectoid steels, for reasons given in Chap. IX, page 312.



FIG. 150.—White cast iron. $\times 100$. (*Metallurgical Laboratory, Univ. of Michigan.*)

White Cast Iron.—Figure 150 shows the structure of a white cast iron containing about 2.3 per cent carbon. This micrograph shows large white areas of eutectic cementite. The dark regions were austenite saturated in carbon (about 1.7 per cent) at a temperature just below the eutectic freezing point, $1,130^{\circ}\text{C}$. On cooling from this temperature to about 700°C ., the carbon in excess of about 0.85 per cent precipitates as Fe_3C (cementite). On cooling austenite so rich in carbon, some of the excess cementite precipitates at the surfaces of the austenite grains, and some along the crystallographic planes of the austenite. Some of

the latter is shown in Fig. 150. The properties of cementite have been described in Chap. VII, page 233.

Carburizing of Steel.—Low-carbon steel heated above about 700° C. in contact with certain carbon-containing materials will absorb carbon at the surface. The carbon slowly diffuses toward the interior, producing a gradient in composition. The higher the temperature the higher will be the carbon content of the surface. This is finally determined by the line *SE* in the iron-



Fig. 151.—Near surface of carburized low-carbon steel, showing fused surface. $\times 100$.

carbon equilibrium diagram. The longer the exposure the deeper will the carbon diffuse. This process is called *carburizing*. The word *carbonizing* is also sometimes used. By varying the time-temperature conditions, “cases” of varying depths and of varying carbon contents can be produced. The steel is in the austenitic state during the carburizing period, at least at the surface where the carbon content is high and, in cooling, the structures typical of the carbon content and austenite grain size are produced. Figure 151 shows the structure of a case-carburized steel prepared by R. R. Abbott, the very high carbon content on the right of the micrograph having been obtained by fusion in contact with graphite. The commercial “cases” are produced while the steel is completely solid and contain carbon less than about 1.5 per cent.

Grain Size Inheritance in Iron and Carbon Steel.—The general effect of inheritance on the grain size of iron and carbon steel has been summarized by one of the authors¹ as follows:

¹ JEFFRIES, ZAY, “Grain Size Inheritance in Iron and Carbon Steel,” *Trans. Am. Inst. Mining Eng.*, vol. 58, p. 669.

1. The ferrite grain size in pure iron, the ferrite and pearlite grain size in hypo-eutectoid steel, the pearlite grain size in eutectoid steel, and the cementite and pearlite grain size of hyper-eutectoid steel are not inherited from the grain size of the mother austenite.

2. The only structural feature that is generally inherited from the austenite of hypo- and hyper-eutectoid steels, on cooling through their transformation ranges, is the position of the excess ferrite or cementite at the austenite grain boundaries, sometimes causing complete and sometimes incomplete networks, which outline the old austenite grain boundaries. Rapid cooling through the transformation range will prevent the inheritance of this structural (network) feature. •

3. The austenite grain boundaries themselves are nearly always effaced in all steels and also in pure iron during the A_r transformations.

4. The grain size refining of steel and iron is brought about by the combined effects of non-inheritance of the transformation products on either heating or cooling, *i.e.*, the austenite transformation products do not inherit their grain size from the austenite on cooling through the transformation range nor does austenite inherit its grain size from the structure which forms austenite on heating.

5. In general, both in iron and in carbon steels, the larger the austenite grain size, the larger will be the grain size of the transformation products on cooling. This, of course, assumes all other conditions constant except the austenite grain size. An exception is found to this general rule in very pure iron, such as electrolytic iron. In this instance small austenite grains may form very large ferrite grains on cooling through A_{r3} . •

6. In iron and steel, the larger the ferrite, cementite, or pearlite grain size the larger will be the austenite grain size on heating above the A_c transformations.

7. The faster the rate of cooling of iron and steel through the A_r transformation range, the smaller will be the grain size of the transformation products.

8. The faster the rate of heating of iron and steel, other conditions remaining the same, the smaller will be the austenite grain size.

9. The greater the temperature gradient during the transformations in iron and steel on heating or cooling, the larger will be the grain size.

10. If the grain size of a transformation product in iron and steel immediately after the transformation is smaller than the equilibrium grain size of that product under the existing conditions, the equilibrium grain size will be established in accordance with the known laws of grain growth.

11. A single grain of any constituent in iron or steel (austenite, ferrite, pearlite), when caused by thermal treatment to undergo one of the polymorphic transformations, must transform from at least one nucleus, but may, and nearly always does, transform from more than one nucleus. • •

In the above discussion the "pearlite grain" refers to an area of lamellar pearlite in which the plates of cementite are approximately parallel or at least continuous. Figure 147, for example, shows the complete cross-section of one pearlite grain and parts of five others.

Pearlite.—Although pearlite consists of ferrite (about 87 per cent) and cementite (about 13 per cent), it is usually regarded as a constituent in steel because its composition is quite definite in any given steel, and under low magnifications its true complexity is not revealed. The characteristic structure of pearlite—the parallel or nearly parallel arrangement of alternate lamellæ of ferrite and cementite—is produced only by cooling through the A_{r1} transformation at a rather definite rate. Cooling more rapidly produces sorbite, while cooling more slowly results in the "divorce" of the pearlite into isolated particles of cementite in ferrite. Although it is only laminated pearlite which produces the play of interference colors under the microscope, and hence is responsible for the name "pearlite," the term is also applied to some of the related structures. Thus, the constituent generally called "sorbite" is sometimes described as sorbitic pearlite when its carbon content is approximately that of the eutectoid. When the lamellæ of pearlite have been broken up and coarsened, but still show by their shape and position evidence of the original laminated structure, the ferrite-cementite aggregate is commonly called *divorced pearlite*. If the cementite particles have assumed fairly spherical forms, leaving little suggestion of the laminated structure, the term "granular" pearlite may be used. Even within the range of laminated pearlite there are wide differences in

the thickness of the lamellæ and in the regularity of their arrangement.

Foreign elements strongly affect the formation of pearlite. Silicon tends to cause straight and parallel lamination, and also accelerates the process of divorce. Manganese and most of the common alloy elements, such as nickel and chromium, exert a directly opposite effect. They retard the decomposition of austenite and hinder the formation and divorce of pearlite. Since some segregation always occurs, in the same specimen of steel, and even in the same field under the microscope, sorbite, lamellar pearlite, and divorced pearlite may be found.

Properties of Pearlite.—The properties of pearlite are measured by those of eutectoid steels in the pearlitic condition. In Table XXII are reproduced, in round numbers, the properties of different varieties of pearlite, as given by Howe and Arnold.

TABLE XXII.—TENSILE PROPERTIES OF PEARLITE

Description of structure	Authority	Tensile strength, pounds per square inch	Proportional limit, pounds per square inch	Elongation in 2 in., per cent	Reduction of area
Sorbitic pearlite, or sorbite	Arnold	157,000	10.0	
Sorbite and sorbitic pearlite	Howe	190,000	83,000	11.0	20
Sorbitic, sublamellar, and lamellar	Howe	135,000	50,000	9.0	13
Normal pearlite (finely laminated)	Arnold	123,000	.	15.0	
Maximum lamellarity	Howe	117,000	58,000	15.0	30
Fine lamellar and beaded	Howe	111,000	56,000	18.0	35
Sublamellar and lamellar	Howe	112,000	41,000	9.5	18
Granular	Howe	90,000	40,000	20.0	40
Coarse lamellar	Howe	108,000	35,000	6.0	10
Laminated (coarse)	Arnold	79,000	5.0	

These figures demonstrate the very great effects produced merely by variations in the arrangement of the cementite constituent. The specific properties of the ferrite constituent in pearlite may be considerably altered by the presence of other elements in solid solution, and it is to be expected that such alteration will be reflected, to some extent, in the properties of the pearlite aggregate. Likewise, the specific properties of the

cementite may be changed by the presence of carbide-forming elements other than iron. It is not probable that such changes will produce appreciable changes in the ordinary mechanical properties of the pearlite, because of the great inherent strength and brittleness of all of the carbides of iron. The mechanical properties of pearlite are therefore partly determined by those of the ferrite constituent, but chiefly by the form and arrangement of the cementite.

The following values may be taken as the average properties of finely laminated pearlite, which is perhaps the most "normal" form:

Proportional limit.....	50,000 lbs. per square inch
Tensile strength.....	120,000 lbs. per square inch
Elongation in 2 in ..	15 per cent
Reduction of area ..	30 per cent
Brinell hardness ..	225

Properties of Ferrite-Pearlite Aggregates.—In many cases the mechanical properties of an aggregate can be represented with some degree of accuracy as arithmetical means of the properties of the elementary constituents. Such representation is fairly accurate in the case of ferrite-pearlite aggregates. The ordinary tensile properties and the hardness of hypo-eutectoid steels in the pearlitic condition are linear functions of the carbon content and, therefore, of the proportion of pearlite. An examination of the results of tests made at various times and places upon the effect of carbon on the properties of steel leads to the conclusion that the relation can be expressed as accurately by straight lines as by curves.

It is well to examine the conditions which result in this fact—that the tensile properties of aggregates of two constituents are approximately linear functions of the proportion of the two constituents present. Four conditions which are found in the case of ferrite-pearlite aggregates appear to be essential:

1. Both constituents are plastic.
2. The more plastic constituent is continuous.
3. The bond between the two constituents is good.
4. Neither constituent is present in submicroscopic grain or particle size.

Cementite-Pearlite Aggregates.—Since the distribution of a brittle constituent chiefly determines its effect upon the aggregate,

this factor must be looked to in considering aggregates of pearlite and cementite. There are three characteristic ways in which cementite occurs in hyper-eutectoid steels:

1. As intergranular envelopes, after very slow cooling from above the upper critical temperature. The effect is then at a maximum and the steel is both more brittle and weaker than a purely pearlitic steel.

2. As plates or spines deposited in the crystallographic planes of the parent austenite grains, during a moderately slow cooling.



FIG. 152.—Cast steel. $\times 100$. (R. R. Studler.)

These plates necessarily decrease the plasticity of the aggregate but, since they do not cause intergranular brittleness, they may increase the strength.

3. As small spherical particles. The excess cementite can be brought into this condition by special heat treatment, such as quenching from above the upper critical temperature, followed by reheating just above A_{c1} and cooling slowly. This type of treatment is generally used only for hardened products, such as steel balls. Whether the matrix is martensite or pearlite, the embrittling effect of the cementite is reduced to a minimum.

Cast Steel.—Steel castings seldom contain over 0.60 per cent carbon and ordinarily contain about 0.30 per cent. Cast steel is constitutionally similar to worked steel, but the grain size is larger because of the absence of the refining effect of mechanical work. Figure 152 is a typical structure of cast steel containing about 0.35 per cent carbon. The old austenite grain boundaries



FIG. 153.—Cast steel, 0.62 per cent carbon, etched with Le Chatelier's reagent. $\times 2$. (V. N. Krivobok in Prof. Sauveur's Laboratory.)

are marked by a definite network of ferrite. There is, however, a marked precipitation of ferrite parallel to the crystallographic planes of the austenite. This structure can be so "refined" by several heatings above the upper critical temperature that it



FIG. 154.—Steel, 0.62 per cent carbon, water quenched from 900° C. Reheated to 600° C. and water quenched. Etched with Le Chatelier's reagent. $\times 2$. (V. N. Krivobok in Prof. Sauveur's Laboratory.)

much resembles that of a worked steel of the same composition which has been normalized. The same general remarks apply to cast steels with different carbon contents.

Even though the structure of cast steel under the microscope shows the constituents called for by the iron-cementite equilibrium diagram, the segregations produced during solidification persist to a certain extent not only after the allotropic transfor-

mation on slow cooling below 700°C . but even after quenching from 900°C . Figure 153 is a macrograph magnified 2 diameters of a 0.62 per cent carbon cast steel, as cast (pearlitic). Figure 154 is a piece of the same steel after quenching from 900°C . and reheating to 600°C . (sorbite). The dendritic structure is undoubtedly caused by the original segregation during solidifica-

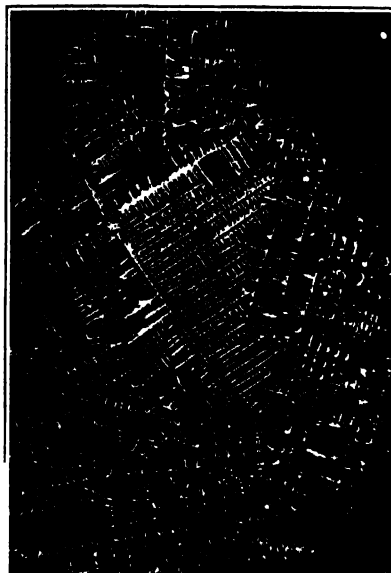


FIG. 155.—Cast manganese steel, 12 per cent manganese, 1 per cent carbon, etched with 4 per cent iodine solution. $\times 22$. (V. N. Krivobok in Prof. Sauveur's Laboratory.)



FIG. 156.—Cast manganese steel, 12 per cent manganese, 1 per cent carbon, etched with sodium picrate. $\times 100$. (V. N. Krivobok in Prof. Sauveur's Laboratory.)

tion. The original grains have been entirely destroyed by the allotropic transformations, but the distribution of certain of the elements has apparently changed but little.

In manganese steel containing about 12 per cent manganese and 1 per cent carbon, Prof. Sauveur has found that the original dendrites are much smaller than in plain carbon hypo-eutectoid steel. The dendrites are revealed under the microscope, however, with certain etching reagents. Figure 155 is a micrograph (magnified 22 diameters) of cast manganese steel etched with 4 per cent iodine solution. Figure 156 is a micrograph of cast manganese steel magnified 100 diameters. The etching reagent was sodium



FIG. 157.—Section of meteorite about natural size. (Dr. R. R. Abbe.)

picrate. The study of dendrites in steel gives information regarding the original grain size after other structural evidences have been destroyed.

Widmannstätten Structure.—When a very coarse-grained, low-carbon austenite transforms to Alpha iron and pearlite in such a manner as to produce marked precipitation of the ferrite at the crystallographic planes of the Gamma iron, the resulting structure is referred to as the *Widmannstätten structure*. This structure was first observed by Widmannstätten in meteorites. Meteorites usually contain considerable nickel, part of which dissolves in the ferrite. The structure is usually so coarse that it can be readily seen with the unaided eye. Figure 157 is a photograph of a meteorite, about natural size, the whole specimen having been originally composed of only three austenite grains.

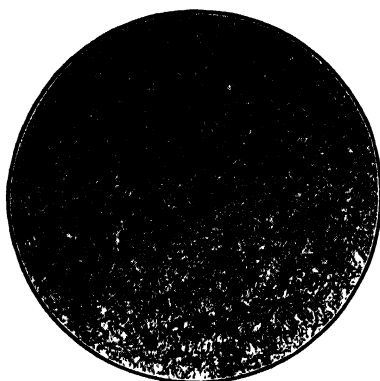


FIG. 158.—Martensite. $\times 250$.
(Homerberg.)



FIG. 159.—Martensite. $\times 500$.
(Homerberg.)

Heat Treatment of Eutectoid Steel.—The structural changes produced in steel by heat treatment are most simple in the case of eutectoid steel, from the standpoint of the number of constituents produced. The effect of change of rate of cooling eutectoid austenite has been briefly discussed above. The faster the rate of cooling the finer is the ferrite-cementite mixture, passing progressively from granular pearlite with very slow cooling to troostite with moderately rapid cooling. When the cooling rate is too rapid for the formation of troostite, martensite forms. The typical structure of martensite is shown in Fig. 158, magnified 250 diameters, and in Fig. 159, magnified 500 diameters. When the cooling rate is not rapid enough to change all of the austenite to

martensite, some troostite forms. Figure 160 magnified 250 diameters, is an example of eutectoid steel quenched at such a rate that about half the austenite transformed to martensite



FIG. 160.—Martensite and troostite.
× 250. (*Homerberg.*)



FIG. 161.—Martensite and troostite.
× 500. (*Homerberg.*)

(light) and half to troostite (dark). Figure 161 is the same as Fig. 160, but magnified 500 diameters. The troostite forms first at the austenite grain boundaries.

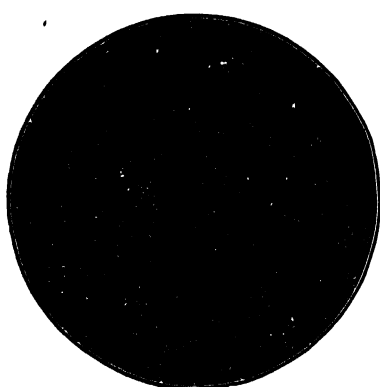


FIG. 162.—Troostite obtained by reheating martensite to 400° C. × 250. (*Homerberg.*)

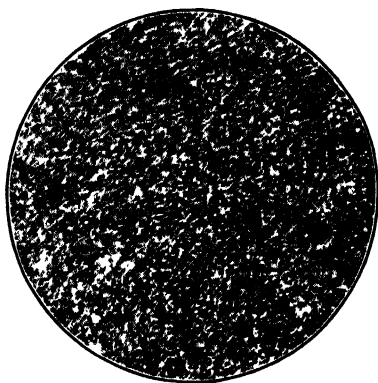


FIG. 163.—Sorbite obtained by reheating martensite at 600° C. × 250. (*Homerberg.*)

When martensite is tempered at temperatures up to 250° C., there is but little apparent change in structure, as observed with the microscope. The polished surface darkens faster when etched than in untempered martensite, as the tempering temperature increases. This darkening becomes very pronounced

when the tempering temperature is about 400°C . This structure is referred to as troostite and is shown in Fig. 162. Troostite etches more rapidly than any other constituent in steel. As the tempering temperature increases above 400°C ., the darkening becomes slower on etching. At a temperature near 600°C . particles of cementite visible under high magnification (500 diameters) appear if the time of heating is sufficient. At the higher tempering temperatures the structure is referred to as sorbite, but there is no sharp dividing line between sorbite and troostite. Figure 163 shows the structure of eutectoid sorbite produced by tempering eutectoid martensite at 600°C .

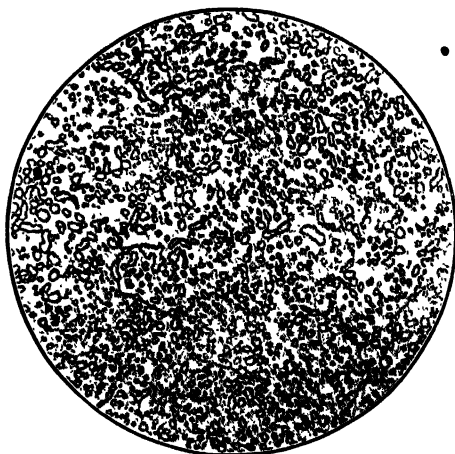


FIG. 164.—Spheroidized cementite in high-carbon steel. $\times 500$. (*Homerberg*.)

When martensite is heated to from 675 to 700°C . for a few hours the cementite globules can often be seen at a magnification of 100 diameters. This structure is granular pearlite, as shown in Fig 164, at a magnification of 500 diameters. The nature and properties of martensite, troostite, and sorbite will be discussed at length in Chap. XII.

Heat Treatment of Other Steels.—Hyper-eutectoid steels containing less than 1.7 per cent carbon and hypo-eutectoid steels are 100 per cent austenite in the *AGSE* temperature-composition area of the iron-cementite equilibrium diagram, page 307. When these steels are quenched at the proper rate from the austenitic condition the metallographic constituents may be the same as in eutectoid steel just described. Martensite may have any carbon content from about 0.20 to about 1.5 per cent. The

products formed by tempering martensite of various carbon contents will have similar variations in composition. A martensite containing 0.20 per cent carbon reheated to 700° C., so as to produce spherical particles, would not, however, be called granular pearlite, because this term applies only to steel of eutectoid composition.

Hypo-eutectoid steels may have free ferrite as a constituent in addition to martensite and the other constituents. If the steel is in the temperature-composition area *GSP*, it will consist of austenite and ferrite. The quantity of each and the composition of the austenite can be ascertained from the equilibrium diagram as described in Chap. IX, page 307. On quenching the steel from this temperature range the ferrite remains unchanged and the austenite may undergo any of the changes described above. If a hypo-eutectoid steel is quenched after *some* of the austenite has changed to pearlite, it is possible to have free ferrite, pearlite, sorbite, troostite, and martensite in the specimen as quenched. On reheating, the martensite changes to troostite at about 400° C. No change occurs in the original troostite until a temperature above 400° C. is reached; it then begins to coarsen toward sorbite. No change in the original sorbite occurs until a temperature above about 500° C. is reached; it coarsens toward granular pearlite. There is no change in the free ferrite or pearlite on heating up to the lower critical temperature, except that long heating just below the lower critical will cause the cementite plates to change to spherical globules. In the example under consideration it is obvious that the austenite must be of eutectoid composition or it would not have begun its transformation to pearlite.

Hyper-eutectoid steels exhibit similarly complicated structural changes. The ideal structure for most tools required to hold cutting edges consists of spheroidal cementite embedded in a matrix of martensite. This structure is produced by quenching hyper-eutectoid steel, with the cementite originally in globular form, from above the lower critical temperature but below the temperature at which all of the cementite will dissolve. The undissolved cementite remains unchanged by the quench and the austenite changes to martensite.

Alloy Steels.—The presence of small amounts of the ordinary alloying elements, nickel, chromium, manganese, silicon, vanadium, molybdenum, and tungsten, as used in the structural alloy

steels, does not materially change the nature of the metallographic constituents. These elements exert their important influence on physical properties largely by altering the rate of the structural changes which have been described. Nickel and silicon go into solution in the ferrite, whereas the other elements form carbides. In the structural steels, that is, steels used for dynamic service, any carbide which may be seen under the microscope would be regarded as cementite. These structural steels usually have a low carbon content because they must possess considerable ductility. In the straight carbon steels, especially with large

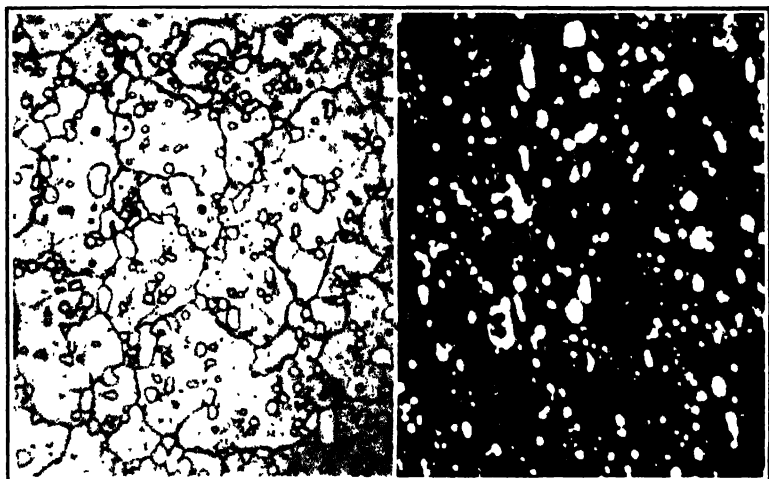


FIG. 165.—High-speed steel quenched from high temperature. $\times 800$. (Bain.)

FIG. 166.—High-speed steel quenched from high temperature and reheated to 700°C . $\times 800$. (Bain.)

sections, it is not possible by quenching to retard the austenite transformation sufficiently to produce as good physical properties as are desired in many automobile and other machine parts. The addition of one or more of the above alloying elements makes it possible to retard the austenite transformation more effectually, and hence produce better physical properties. In these structural parts the steel is usually tempered or “drawn” after quenching so as to produce sorbite. Spring steel contains more carbon than structural steel and after quenching it is tempered to produce troostite.

High-speed Steel.—High-speed steel is an alloy tool steel containing usually about 18 per cent tungsten, 4 per cent

chromium, 0.7 per cent carbon, and 1 per cent vanadium. In this steel there appears a new carbide containing iron, tungsten, and carbon, and probably chromium and vanadium. This carbide exists in such large quantities that it is not all dissolved in the austenite even at the melting point of the steel. Figure 165 shows the structure of such a steel quenched from 1,288°C. (2,350° F.). The grain boundaries represent old austenite grains which, however, have partly changed to martensite. The carbide particles can be readily seen. Figure 166 shows the same steel after quenching from 1,288° C. (2,350° F.) and reheating at 704° C. (1,300° F.). The structure is practically troostite and complex carbide. The alloying elements have so changed the transformations which take place on tempering that the troostite forms only at a temperature about 300° C. (550° F.) higher than in the martensite of straight carbon steels. The nature of high-speed steel will be considered in Chap. XII.

Properties of White Cast Iron.—When an iron-carbon alloy containing more than about 2 per cent carbon solidifies and cools

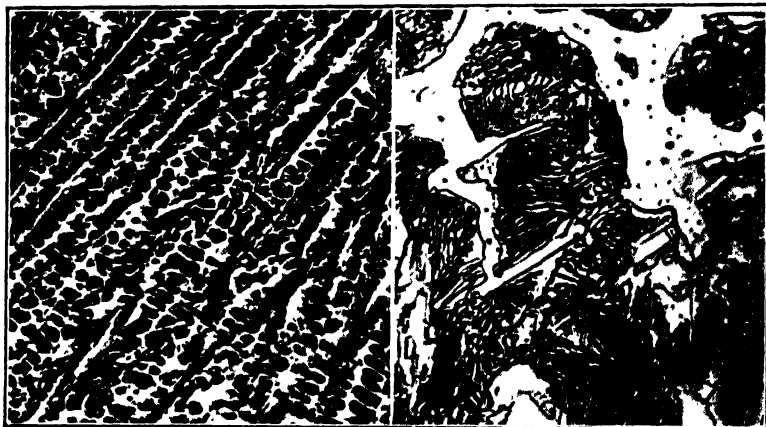


FIG. 167.—White cast iron.
× 100. (*Payne-National Malleable
Castings Co.*)

FIG. 168.—White cast iron. × 500.
(*Payne-National Malleable Castings
Co.*)

to ordinary temperature without the formation of graphite, the material is referred to as white cast iron. The fracture is bright with a high metallic luster. Such a fracture is called “white,” and hence the origin of the name. It has a very characteristic structure consisting of free cementite and pearlite. The white constituent in Fig. 167 is cementite and the dark is pearlite.

Figure 168 shows the same material at 500 diameters. The typical structure of the pearlite can be plainly seen.

Owing to the great hardness of cementite and its quantity and arrangement, white cast iron is very hard and brittle. It is used for wire-drawing dies and for certain other dies. Chilled car wheels have the white iron structure on the wearing surface. This is produced by cooling the surface at a rate which will prevent graphitization. Rolls are commonly made with white iron surfaces.

Malleable Cast Iron.—White cast iron of certain composition heated for some time at about 850° C. (1,562° F.) and cooled

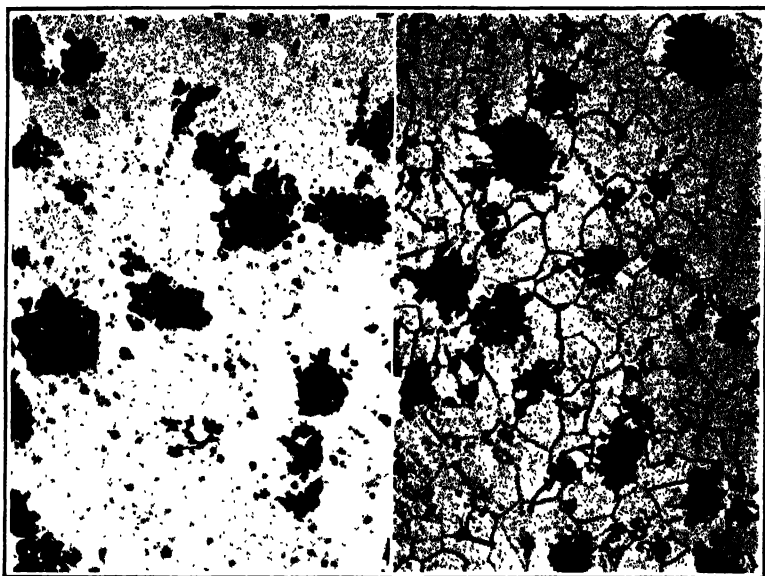


FIG. 169.—Malleable iron, as etched.
× 200. (*Payne-National Malleable Castings Co.*)

FIG. 170.—Malleable iron, etched.
× 200. (*Payne-National Malleable Castings Co.*)

very slowly to a temperature below about 700° C. (1,292° F.) changes to malleable cast iron. When the process is carried out to completion, all the cementite is changed to graphitic carbon. Figure 169 shows the structure of malleable cast iron before etching. The black spots are partly carbon and partly holes. The carbon of malleable cast iron is referred to as “temper” carbon. The white portion is ferrite, containing, of course, most

of the other elements in solid solution. Figure 170 shows the structure after etching to bring out the ferrite grain boundaries.

A composition of white cast iron to yield an average tensile strength, after malleable annealing, of about 52,000 lb. per square inch and an elongation of 15 per cent or over is given by Touceda as follows: carbon 2.30 to 2.35 per cent; silicon 0.90 to 0.95 per cent; phosphorus 0.18 per cent; sulphur 0.06 per cent; and manganese 0.23 per cent. In so far as strength and hardness are concerned, the temper carbon has about the same effect as if the spaces occupied by it were holes. The ferrite is strengthened and hardened by the silicon and phosphorus in solution.

Gray Cast Iron.—When the silicon content is high (1.25 to 3.25 per cent), iron-carbon alloys containing more than about 2.5 per cent of carbon cannot be cast under ordinary cooling conditions of sand molds without the formation of flakes of graphite. Such material has a gray fracture and is called “gray cast iron” or, more commonly, “gray iron.” Structurally, gray iron may be considered as a steel matrix in which graphite is embedded as an impurity. The matrix may be nearly all ferrite in rare cases, but usually is that of a hypo-eutectoid steel. The matrix may, however, be eutectoid or hyper-eutectoid.

Figure 171 shows the structure of gray iron without etching. The black gashes are graphite. The graphite is about as effective as holes, as regards mechanical strength in tension. It is quite certain that graphite does not adhere strongly to the matrix. This fact, coupled with its commanding position, makes gray iron quite weak in tension. On the other hand, graphite offers the usual resistance of a solid material to reduction in volume by hydrostatic pressure. Compression of a mass of cast iron, in effect, puts hydrostatic pressure on the graphite particles. Gray iron is, therefore, not particularly weak in compression.

Gray iron varies in carbon content from about 2.5 to 4 per cent, in silicon from 1.25 to 3.25 per cent, and in phosphorus from 0.10 to 1.5 per cent. The manganese is usually under 1 per cent and sulphur under 0.15 per cent. High phosphorus content gives rise to the formation of a ternary eutectic called *steadite*, containing iron phosphide (Fe_3P) and cementite. Figure 172 is a gray iron, unetched, showing, besides the large flakes of graphite and the ordinary steel matrix, the iron phosphide-iron carbide eutectic. This iron contains in per cent, carbon 3.52, silicon 2.53, phosphorus 0.409, sulphur 0.027, and manganese 0.42.



FIG. 171.—Gray cast iron, unetched. $\times 100$. (*Zimmerschied-General Motors.*)



FIG. 172.—Gray iron containing phosphorus, unetched. $\times 500$. (*Zimmerschied-General Motors.*)



FIG. 173.—Cylinder iron containing more than 1 per cent phosphorus, etched.
 $\times 100$. (*Zimmerschied-General Motors.*)



FIG. 174.—Cylinder iron containing more than 1 per cent phosphorus, etched.
 $\times 500$. (*Zimmerschied-General Motors.*)

Figure 173 shows an etched specimen of a cylinder iron containing somewhat over 1 per cent of phosphorus. Figure 174 is the same iron at higher magnification. The phosphorus constituent is hard and its presence adds to the hardness of the iron.

The areas commonly recognized under the microscope as graphite may, in reality, consist of fine laminations of ferrite and graphite. This is usually the case when graphitization has taken place after solidification. Such areas may be regarded as ferrite sponges. The effect of graphite on physical properties is obviously dependent on the size, shape, and quantity of particles present. The extreme forms are represented by the large flakes found in soft gray iron, which render the aggregate very weak and brittle, and by the smaller rounded globules found in annealed malleable cast iron. This form has a minimum effect on the properties of the aggregate. Between these extremes graphite assumes a continuous series of shapes and sizes, according to the conditions at the time of its formation. In general, it may be said that the coarse, flaky condition of graphite is more pronounced the more rapid its formation. Zimmerschied and others consider that a pearlite matrix is the best for strength. A cast iron containing 2.94 per cent total carbon, 0.54 per cent combined carbon, 3.12 per cent silicon, and 0.137 per cent phosphorus had a eutectoid matrix and showed an average tensile strength of 42,000 lb. per square inch. Some of the soft irons may show strengths less than 20,000 lb. per square inch. The quantity and distribution of graphite is, however, the important factor in determining the properties of gray iron. In general, the strength of gray iron is not more than one-third that of the matrix free from graphite, and in all gray irons the ductility is practically nil.

The Obstruction Principle.—It has long been recognized that the presence of a hard and strong constituent in an alloy may strengthen it by opposing the “flow,” or slip, of the weaker constituent. Just as slip is opposed at the grain boundaries of a pure metal by the change in orientation, it may be opposed to a still greater extent if the material at the grain boundary possesses, in addition to its different orientation, a specifically greater hardness.

This mechanism of hardening, which has been described as the “obstruction principle,”¹ refers particularly to reinforcement of a

¹ See discussion of the obstruction principle in “Metallography of Steel and Cast Iron,” by H. M. HOWE.

continuous plastic matrix by grains of a stronger constituent which are similar in size to the grains of the matrix. The grains of the matrix are strengthened by *external* support.

If the hard constituent forms a continuous network around grains of a plastic constituent, the interference to slip may be quite marked. The aggregate is harder, other conditions being the same, the greater the quantity of hard constituent. Refinement of the particle or grain size of the constituents also causes increase in hardness. When the aggregate consists of a hard constituent surrounded by a plastic constituent, the tensile strength and hardness are greater than those of the plastic constituent by itself. The reason for the increased hardness seems obvious, but the reason for the increased strength is not so simple. An aggregate of pearlite and ferrite, in which the ferrite is the continuous constituent, will serve as an example of this general case. When the aggregate is loaded in tension to the tensile strength of pure isolated ferrite, why does not rupture take place? The ferrite by itself would have about 85 per cent reduction of area at the fracture. This reduction is necessary in order to produce rupture at the low tensile strength of 38,000 lb. per square inch; it facilitates the process of rupture by degrees. The ferrite of the ferrite-pearlite aggregate is supported between walls of harder pearlite and cannot locally reduce in area much without movement in the pearlite. The harder pearlite therefore helps the ferrite to resist rupture by bringing more atomic bonds into play simultaneously to resist deformation and rupture. If the ferrite were a structureless amorphous substance, the pearlite could produce only a mild strengthening effect, by a sort of frictional resistance to flow, but the ferrite is crystalline and yields only by slipping on its crystallographic planes of weakness, and such slip is opposed by the rigidity of the pearlite. It has recently become evident that metals can be hardened to a still greater degree by a hard substance dispersed as fine particles *within* the grains.

Aging of Duralumin.—A very important step in the development of the theory of hardening by hard substances highly dispersed is the study of the light aluminum alloys of the "duralumin" type, by Merica, Waltenberg, and Scott.¹ The following

¹ MERICA, P. D., WALTENBERG, R. G., and SCOTT, H., "Heat Treatment of Duralumin," *Bull. Am. Inst. Mining Eng.*, p. 913, June, 1919; *Chem. Met. Eng.*, vol. 21, p. 551 *et seq.*

is typical of the composition of these alloys: copper, 4.0 per cent; magnesium, 0.5 per cent; manganese, 0.5 per cent; aluminum (commercially pure), remainder.

These alloys in the rolled or forged condition can be very materially hardened by a heat treatment consisting of quenching from about 500° C., followed by aging for several days at ordinary temperatures. The hardness and strength immediately after quenching are somewhat greater than in the "annealed" condition and, on aging, increase spontaneously about 50 per cent.

Merica, Waltenberg, and Scott base their explanation of this hardening on the variation of the solubility of the compound, CuAl_2 , in aluminum with temperature. Figure 106 is a portion of the equilibrium diagram of the aluminum-copper system, showing the solubility curve of CuAl_2 in aluminum. It will be noted that the solubility of the compound decreases from about 4 per cent (copper) at 500° C. to less than about 2.5 per cent at room temperature. A piece of duralumin examined microscopically immediately after quenching shows a "solid solution" structure—that is, a structure free from visible particles of CuAl_2 . After the alloy has aged so that the hardness and strength have greatly increased, the structure is apparently unchanged. There is reason to believe, however, that there has occurred during aging a precipitation of CuAl_2 in the form of particles of submicroscopic size, to correspond to the diminished solubility of the compound at the lower temperatures. Quoting from the paper referred to, by Merica, Waltenberg, and Scott:

Upon heating a specimen of duralumin that has been quenched from 500° C., but not aged, an evolution of heat occurs at from 250 to 275° C.

No thermal change takes place upon cooling the same specimen, provided it has not been heated beyond 520° C. Upon reheating the same slowly cooled specimen, no evolution of heat is found corresponding to that upon the first heating. Without doubt, therefore, a chemical reaction takes place at 250 to 275° C. upon heating the quenched sample, with evolution of heat—i.e., indicating the formation of stable from unstable phases, not a transformation of stable to other stable phases, the two systems being in equilibrium during the transformation. Such a transformation must take place with heat absorption upon raising the temperature.

A specimen that has been quenched and aged at from 100 to 150° C. to secure maximum hardness shows little or no evolution of heat upon

heating. Whatever may be the chemical reaction that is indicated on the first heating curve of a quenched specimen, it has taken place during the aging of the specimen, during which the hardening also occurs; stable phases have formed and the subsequent heating curve shows no arrest corresponding to that of the quenched specimen.

This chemical reaction can hardly be other than the precipitation of CuAl_2 from its supersaturated solution in aluminum, although direct visual evidence bearing on this question is also lacking. . . .

Although it cannot be directly proved that the thermal arrest at about 250°C . noticed upon heating a quenched unaged specimen of duralumin is due to the precipitation of CuAl_2 , no evidence directly contradicts this assumption, which is in entire accord with our knowledge of the equilibrium within the alloy, and this arrest cannot be assigned to any other phase change.

It has been shown by many previous investigations and confirmed by the authors that aluminum undergoes no transformation in the solid state between ordinary temperatures and its melting point. No other phase changes could occur in the main mass of duralumin, the grains of solid solution, therefore, except those of solution or precipitation of FeAl_3 , of the X compound, of CuAl_2 , of Mg_2Al_3 , or of Mg_2Si , within the grains. Aluminum, which contains the same amounts of FeAl_3 and of the X compound as does duralumin, is not altered by heat-treatment as is duralumin, nor does it show a reverse heat effect upon heating as does the latter. This heat effect must, therefore, be due to the precipitation either of CuAl_2 , Mg_2Al_3 , or Mg_2Si . But the alloys containing only magnesium in amounts up to 3 per cent also do not harden upon aging. There remains only the precipitation of CuAl_2 with which to explain this heat effect.¹

The theory outlined above of the mechanism of the hardening of duralumin during aging most readily explains the interesting fact discovered by Mr. Blough and confirmed by the authors that the amount of hardening during aging increases as the temperature of quenching increases. At higher quenching temperatures more and more CuAl_2 is dissolved in solid solution. After quenching, the CuAl_2 is in excess of its solubility; the higher the quenching temperature the greater is the excess, and this is precipitated during aging. The hardening is in proportion to the amount of the highly dispersed CuAl_2 formed.

If this theory is accepted for the moment, it is interesting to consider the effect of degree of dispersion upon hardness in the case of a solid solution, in this case of CuAl_2 in aluminum. Duralumin immediately after quenching is generally softer than it is in the annealed condition.

¹ Alloys containing magnesium and silicon, without copper, do harden on aging, and it has been shown that this hardening is very probably due to precipitation of Mg_2Si . (Present Authors' Note.)

Thus, alloy C-11, in the form of sheet, gave the following values of hardness.

	ANNEALED AT 300°	QUENCHED BUT NOT AGED	QUENCHED AND AGED 8 DAYS
Scleroscope hardness, magnifying hammer	17	16	35

This is probably due to the fact that a specimen, as ordinarily cooled after annealing, still contains some dissolved CuAl_2 in excess of its solubility; the material hardens slightly during cooling. Specimens cooled extremely slowly give a scleroscope hardness of from 7 to 10, much lower than that of the quenched, unaged ones.

Upon aging a quenched specimen at 200° C., for example, the hardness first increases to a maximum and afterward decreases. During that aging there has been first a formation of fine nuclei of CuAl_2 , followed by coalescence of these particles into ones of larger size. There is, therefore, a certain average size of particle of CuAl_2 for which the hardness of the material is a maximum; atomic dispersion of the solute, CuAl_2 , is not the dispersion that produces the maximum hardness, but some intermediate one between it and that at which the particles become visible by ordinary means.

An important point in this theory of the hardening of duralumin is the conclusion that there is a certain average size of particle which produces maximum hardness, any size either larger or smaller causing less hardness. This is opposed to the idea previously held that a given amount of a substance added to a metal produces the greatest possible hardening effect when it is in *solution*—that is, when it is in the highest possible state of dispersion. The degree of dispersion conducive to maximum hardness may conveniently be designated by the term “critical dispersion.” Dispersions finer than this may be called “sub-critical,” and those coarser “super-critical.”

It is also important to note the magnitude of the hardening effect in duralumin. It is possible to increase the hardness of pure aluminum approximately tenfold by producing within grains of an aluminum-copper solid solution a critical dispersion of hard particles. This hardening cannot be referred to any of the mystic causes sometimes assigned in the case of steel. The only conceivable explanation is that it is due to the presence of a vast number of very small, hard particles dispersed throughout the grains of aluminum, which probably retain some copper in true solid solution.

These conclusions regarding the hardening of duralumin naturally suggest seeking analogies in other alloy systems.

Merica and his coauthors called attention to the case of steel, pointing out a similarity to duralumin in that the decomposition of a solid solution into particles of submicroscopic size (ferrite and cementite) is involved and also in that some steels (very high-carbon steels and high-speed steels) show, on tempering, an *increase* in hardness, followed by the usual decrease. The theory advanced for the hardening of duralumin did not include any explanation of the mechanism by which the particles of CuAl_2 cause hardness. Some conception of this mechanism is necessary to any extension of the theory.

The present authors have attempted to analyze the mechanism of this hardening effect, so that the necessary conditions could be defined for all cases. Such analysis involves the explanation, first, of how one constituent dispersed within another produces such great hardness, and, second, of why there is a critical dispersion or size of particle which produces maximum hardness.

Easy Slip in Magnetized Plates.—In duralumin the aggregate is composed of a ductile, relatively weak matrix—aluminum—greatly strengthened by the presence of small, hard, *disconnected* particles of CuAl_2 . The strength attained in the duralumin must be derived from the inherent cohesion of the continuous aluminum matrix. There is no conceivable way in which a few per cent by volume of a strong constituent in disconnected particles could impart a new element of cohesion of the magnitude actually obtained. Their action must consist in rendering more effective the cohesion latent in the aluminum. The logical inference is that this is accomplished by the elimination of extended planes of weakness—that is, by slip interference.

Figure 175 represents a section through a crystal, the fine parallel lines representing a set of planes of easy slip. It may assist in obtaining a concrete conception of the mechanical conditions to consider a stack of iron plates placed in a strong magnetic field at right angles to their surfaces. It would be very difficult to pull these plates apart by a straight tensile effort, but comparatively easy to separate them by sliding them over each other. This stack of plates presents a rather close analogy to the conditions obtaining in a ductile crystal, especially in that the forces which hold the atoms of a crystal together are probably electromagnetic in character.

In separating the magnetized plates by a straight pull it is necessary to overcome the entire magnetic attraction at once,

whereas in sliding the plates the magnetic force is overcome only at the edges and then gradually by small increments. The principal resistance due to sliding is the frictional resistance of the plates due to the pressure. In order completely to separate the portions of a crystal on opposite sides of a plane of slip by a direct tensile pull, it would be necessary to break simultaneously all the atomic bonds on the plane. This would require a force equal to the absolute cohesion of the metal. The two portions can move with respect to each other on the slip plane without permanent rupture of any considerable proportion of the atomic bonds. Of course, extended slip separates the atoms from their old neighbors, but cohesion bonds are established with their new neighbors. The separation of the magnetized plates by a direct pull results in a "brittle" fracture with a minimum work of rupture. When the plates are separated by sliding, the work of rupture is increased by an amount equal to the frictional losses. Similarly, when a crystal is fractured in a brittle manner, the work of rupture is a minimum, whereas in a ductile fracture the work of rupture is markedly increased, due to the friction at planes of slip.

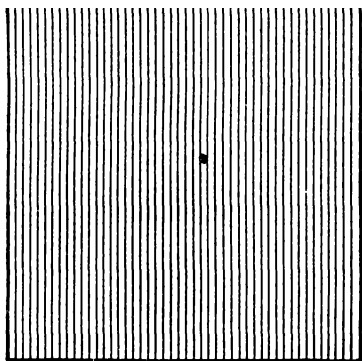


FIG. 175.—Set of planes of easy slip in a crystal having no internal keys.

Small, Hard Particles Act as Keys.—Figure 176 shows an ideal section through a crystal in which it is supposed that a hard, strong substance is dispersed in the form of substantially spherical particles. These particles are supposed to be about equal in size, but of course the circles cut by the plane of the section should be of different sizes according to the distance of this plane from the centers of the spheres. It will be noted that there is not a single plane of easy slip which does not encounter at least one of these hard particles. Under the action of an external load tending to produce slip along these planes, the hard particles must act as *keys*, mechanically obstructing any motion along the planes as a whole. The result is increased elastic limit, hardness, and strength.

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Now suppose all the hard particles to be gathered into a single large particle, as shown in Fig. 177. Although the size and strength of the "key" are greatly increased, there are many planes of weakness left without any reinforcement. The single large particle does not interfere with slip on these planes. It is easily seen that the strengthening effect of the hard particles increases with their *number* and not with their size. Even in case all possible planes of slip are keyed at some points, more effective slip interference must result from diminishing the size and increasing the number of the particles. Thus the rule that the hardening effect of a given amount of hard, dispersed substance is greater the smaller the particles. This rule must reach a

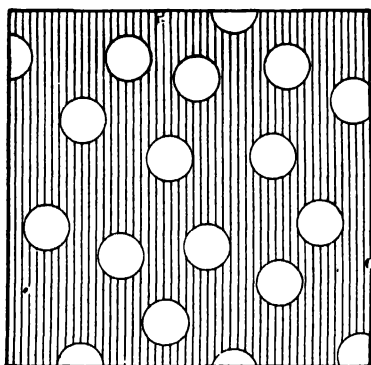


Fig. 176.—Slip planes keyed by hard particles.

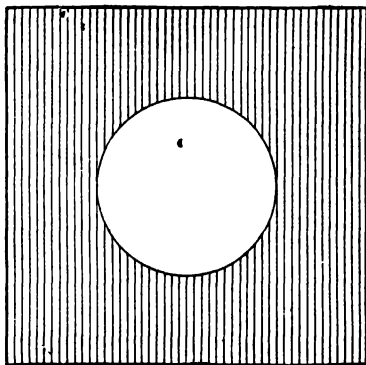


Fig. 177.—Hard constituent gathered into a single large particle leaving many planes unkeyed.

limit as the particles approach atomic dimensions. It is not known how small a crystal may be and still possess the characteristic hardness and strength of the substance.

Hardening of Solid Solutions.—Consider the strength of true solid solutions or atomic dispersions from the point of view of slip interference. Planes of weakness are present just as in the pure metal or solvent. At intervals, the succession of atoms of solvent is interrupted by an atom of the solute. At each point where an atom of the solute occurs there is an increased bond, or, it might be said, pressure, on the plane of potential slip, due to the greater force of attraction between the unlike atoms. This constitutes in effect a key, very much as do the crystalline particles of CuAl_2 in aluminum. The planes are seemingly "spot welded" together by the atoms of the solute.

The experimental evidence indicates that the formation of crystalline nuclei of CuAl_2 in duralumin, from the solid solution of copper in aluminum, causes an increase in hardness and strength. If the key action of the atomically dispersed copper were equivalent to that of the crystalline particles of CuAl_2 , it would not be expected that this would be the case, since the hardness should increase as the number of keys increases. It is quite natural to suppose that the attractive forces of the copper and aluminum atoms for each other are not brought fully into play until the atoms are arranged in their most stable arrangement—that of the compound. The key formed by the little group of aluminum atoms surrounding the copper atoms in the solid solution is more easily sheared through than is a particle of crystalline CuAl_2 . The critical dispersion for maximum hardness should, therefore, consist of the smallest possible particles having the characteristic crystallinity of the compound. If particles are classified according to their diameters in terms of atoms, the following probably represents approximately the sizes involved:

1 atom diameter	... Solid solution	Somewhat hard
10 atom diameters	... Critical dispersion	Hardest
1,000 atom diameters	... Smallest visible particles	Somewhat soft

Number of Keys in a Duralumin Crystal.—Take for an example the hardness changes in a duralumin alloy containing 4.5 per cent copper. This alloy would contain 2 atoms per cent of copper or 8.33 weight per cent of CuAl_2 , assuming that all of the copper is present as that compound. This would be at most 5.4 per cent CuAl_2 by volume; actually, it is less than that amount, inasmuch as some of the copper will always be in solution. When the worked alloy is heated to a temperature at which all of the copper is in solution and then quenched, the hardness will be about 70 Brinell. The copper is probably in atomic dispersion. On aging, the hardness can be increased to about 130 Brinell as the CuAl_2 precipitates and the particles reach critical size. By very slow cooling from high temperatures, the hardness can then be reduced to about 50 Brinell. Such a hardness is produced only after the CuAl_2 particles have reached relatively large sizes.

Tensile strength varies with the hardness. The plasticity is the greatest in the annealed material, quite considerable in the

freshly quenched condition, and least when the CuAl_2 particles are present in critical size. The high plasticity accompanying atomic dispersion of copper would be expected, because the areas of potential slip planes will depend on grain size only. The interference to slip is greater than in pure aluminum; it is due to the greater pressure on and greater roughness of the slip surfaces.

An average-sized grain of duralumin would have about 2,000,000,000 atoms of copper on each potential slip plane. Although it is not known exactly the percentage of the copper precipitating as CuAl_2 during aging, for convenience, it can be considered as 75 per cent of that present. Assuming now that the CuAl_2

particles have reached an average size of $\frac{1}{10,000,000}$ -in. diameter there will still be 500,000,000 copper atoms on each of the above planes and, in addition, each plane will be keyed with the relatively hard CuAl_2 particles at 35,000,000 to 40,000,000 places. This condition corresponds nearly to critical dispersion. By the time the CuAl_2 particles have reached an average diameter of a hundred-thousandth of an inch, each of the above planes will be keyed in about 3,500 to 4,000 places; if the diameter were further increased 100 times, only about three planes out of eight would be keyed at all!

The presence of a given amount of hard substance in large particles produces excess slip interference locally, but leaves portions of the metal in a weak condition. Cohesion of the mass as a whole is, therefore, gained by subdivision of the key material into many particles distributed as uniformly as possible. The weak links of the chain of slip planes are thus strengthened at the expense of the strong ones. Plastic deformation in such a material produces an intricate system of slip planes determined by the number and size of the particles. In many places rupture cannot follow the easy crystallographic planes, but is forced to take place in unfavorable directions. The quantity of dispersed substance may be so great that the resistance to slip becomes equal to or greater than the direct rupturing strength of the atomic bonds, and brittleness accompanied by relatively great hardness will result.

Figure 178 is a micrograph of high-carbon steel in which the cementite has been coarsely spheroidized and which has been polished and deformed cold in a vice. It will be noted that the slip avoids the cementite and that the surfaces of slip are

rough. The appearance is intricate as opposed to the systems of regular slip planes in nearly pure metals shown in Figs. 179 and 180. As compared to critical size, the particles of cementite shown in Fig. 178 are very coarse. Each of the larger particles of cementite shown in this micrograph would have to be subdivided into about 1,000,000,000 particles to reach critical dispersion. The intricacy of the system of slip planes would correspondingly increase.

Some criticism has been made regarding the above interpretation as to the reason for a certain size of particle producing

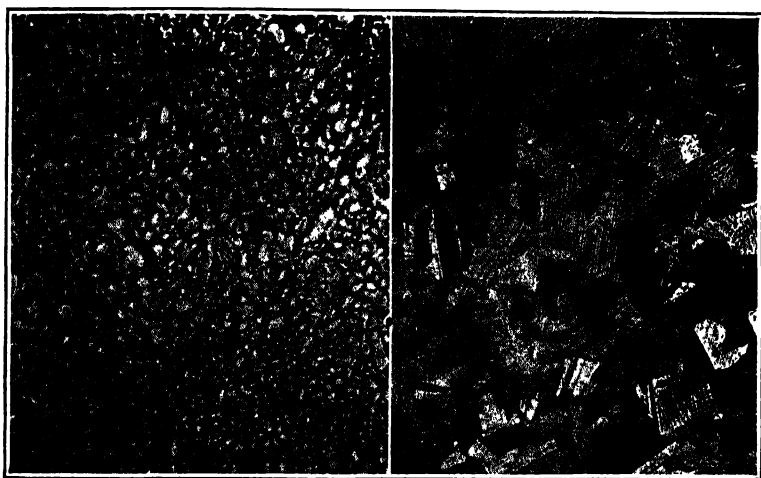


FIG. 178.—Plastic deformation in high-carbon steel with spheroidized cementite. $\times 650$.

FIG. 179.—Slip bands in copper containing a small percentage of copper oxide. $\times 50$.

maximum hardness. Rosenhain expressed the opinion that the precipitation of a compound caused great disorder or distortion in the crystalline lattice of the matrix and that the increased hardness is due to such distortion. It is also Rosenhain's view that the hardness of a solid solution is due to the distortion of the crystal lattice of the solvent by the atoms of the solute. The more solute present the greater the distortion, and hence the greater the hardening effect. According to this conception, the crystal lattice of the matrix should become softer by the precipitation of a hard compound because fewer solute atoms will remain to cause distortion. No matter what explanation for the hardness of a solid solution is preferred, it is a fact that the greater

the amount of solute present in solution the greater the hardness of that solution. Removal of solute atoms should, therefore, soften the matrix. In duralumin it is certain that the matrix is markedly softened when the particles of precipitated compound are decidedly super-critical in size. There is no reason to suspect any other effect on the hardness of the matrix itself when the particles are of critical size.

Merica has called attention to the fact that a given quantity of hard substance dispersed in a crystal will expose the same shearing area on the slip planes regardless of the particle size. He draws the conclusion that a given quantity of hard constituent should have the same keying effect regardless of the particle size. In view of the fact that a given quantity of a hard constituent actually has a greater hardening effect when present in particles of a certain size, Merica suggests that the cause must be looked for in the higher surface tension forces of the small particles, which give them an effective sphere of influence beyond their true diameters.

It is the authors' opinion that it is a mistake to conclude that the keying effect of hard particles is proportional to the total areas intersected by potential slip planes. It is probably true that the shearing strength through the hard particles themselves, along any given plane, is the same regardless of the particle size. *The very small hard particles are, however, never sheared through.* The shearing strength of these particles is so much greater than that of the adjacent matrix that slip occurs in the latter.

Consider the effect of keying in a hypothetical extreme case. Suppose a 1-in. cube of steel of eutectoid composition has the 13 per cent of cementite concentrated into one sphere at the center. A Brinell hardness or scleroscope hardness test at the surface would indicate practically the hardness of ferrite. The shearing strength of the cementite itself does not come into play. The potential slip planes near the cementite particle and intersected by it are keyed as effectively as in the hardest steel. In fact, the cementite itself could have a shearing strength ten times its real value without changing the measured hardness. Now, if the cementite be subdivided into 1,000,000,000 particles of equal size and distributed uniformly throughout the cube, the centers of adjacent particles would be approximately one one-thousandth of an inch apart. In either the Brinell or scleroscope test some of these particles would be in the deformed areas

and would interfere with slip on the crystallographic planes of the ferrite. The hardness would be increased. Greater subdivision of the particles will reduce the size of unkeyed areas and will necessitate a more devious path of slip for a given amount of deformation, which is another way of saying that slip is more interfered with or that the hardness will be increased. Decreasing the size of hard particles within a crystal acts somewhat like decreasing grain size in a pure metal or solid solution; in either case the area of slip on any one plane is reduced.

In duralumin, for example, it is the obvious conclusion that the inherent resistance to slip in the matrix is a maximum in the material as quenched, *i.e.*, with a maximum number of foreign atoms in solution. The potential slip planes, however, are large in area, being determined, as in any pure metal or solid solution, by the grain size. The resistance to slip in the matrix itself decreases as precipitation of the foreign atoms proceeds, but the keying effect more than compensates for this tendency to soften, so that the net result is an increase in hardness.

Adhesion between Constituents.—While the CuAl_2 and Fe_3C particles probably have rather strong adhesion for the aluminum and iron respectively, such adhesion need not obtain in order to produce hardening. Copper oxide, often present in copper, should have very little adhesion for the metal, but when it is present in the form of globules within the copper grains it produces a strengthening effect. Antisell¹ states that 0.2 per cent oxygen (1.8 per cent Cu_2O) increases the tensile strength of annealed copper over 10 per cent. Figures 179 and 180 show a small quantity of Cu_2O . The particle size is large as compared to critical dispersion. It will be noted that the slip planes in Fig. 180 have a tendency to extend completely across the grains. Yet slip planes in general avoid the Cu_2O particles or are faulted or stopped by them. This represents the first stages of slip interference.

Thorium dioxide probably has little adhesion for tungsten but, when 1.5 per cent by volume is present as particles within the grains, the tensile strength is increased, in the temperature regions within which the metal is ductile. The presence of the thoria also has the effect of causing a greater increase in tensile strength for a given amount of working below the recrystallization

¹ ANTISELL, FRANK L., "Relationship of Physical and Chemical Properties of Copper," *Trans. Am. Inst. Mining Eng.*, vol. 74, p. 432, 1920.

temperature than in pure tungsten. The cases of Cu_2O in copper and ThO_2 in tungsten are important, because they give positive evidence of the strengthening effect of these mixtures in which a weakening might be expected, due to decrease of the effective cross-sections of the metals.



FIG. 180.—Slip bands in copper containing a small percentage of copper oxide.
× 250.

In all of the cases mentioned above, the hardness has been produced by dispersing *hard* particles within relatively large grains of metal. It should not be expected that *soft* particles will produce hardening, because the “keys” of soft substance would shear and thus assist rather than oppose slip. The term *soft* is used here in the relative sense only.

CHAPTER XI

GENERAL CONSIDERATIONS ON THE HARDNESS OF METALS

In *Chemical and Metallurgical Engineering*, June 15, 1921, the authors put forward a general theory of the hardening of metals, under the title, "The Slip Interference Theory of the Hardening of Metals." Parts of this theory have been discussed in detail at various points in preceding chapters of this book. It is the purpose of this chapter to present a resumé of the general theory of hardening which will assemble this scattered information, and also serve as a basis for the highly specialized discussion of the hardening of steel given in the next chapter.

Definition of Hardness.—The general terms "hardness" and "strength" connote a number of more specific physical properties. The most definite of these is the proportional limit or, what is practically the same thing, the elastic limit. The common measure of the strength of a material is its "tensile strength," or the maximum intensity of tensile stress endured before rupture, calculated on the original cross-sectional area of the test piece. This is obviously a more complex property than the elastic limit. Hardness may mean resistance to indentation, as measured by the Brinell test, resilience, as measured by the Shore scleroscope, scratch hardness, cutting hardness, resistance to machining, or some other special kind of hardness. All of these properties may be embraced in the general definition: *Hardness is resistance to permanent deformation.*

Fundamental Cause of Hardness.—Metals owe their resistance to deformation to the forces between the atoms. These forces are both attractive and repulsive. Repulsive forces are manifested by the resistance of metals to hydrostatic pressure by which the atoms are forced closer together in all directions. Under direct tension the distances between atoms are increased in the direction of the load and decreased at right angles, that is, in the direction of the secondary compressive stresses. There is no condition of loading corresponding to a negative hydrostatic

pressure, under which the interatomic distances would be increased in all directions.

Any permanent deformation of a metal involves changes in the relative positions of some of the atoms, and, therefore, the breaking, temporarily at least, of some interatomic "bonds." The rupture of any material, whether with or without permanent deformation, also involves the breaking of interatomic bonds. The greatest possible resistance that a material can offer to deformation or rupture is the summation of all the interatomic bonds on a plane through the specimen normal to the stress, a summation which may, for convenience, be termed the "absolute cohesion" of the material. Actually, such a summation of forces is never realized, because rupture always takes place by degrees, and the breaking of atomic bonds is not simultaneous. The tensile strength of a material merely represents the maximum number of atomic bonds that come into play simultaneously during the test.

Great Inherent Cohesion of Metals.—Absolute cohesions of metals are far in excess of the values obtained for tensile strength. A qualitative illustration of this fact may be found in a consideration of some properties of pure iron. The tensile strength, after hot rolling, is about 40,000 lb. per square inch, a value representing, as usual, the maximum load divided by original cross-section. If the actual reduced area of the test piece is measured throughout the progress of the test, and the stress computed on this basis, a value will be found for the maximum stress which is much higher than the tensile strength. The maximum stress will then be about 80,000 lb. per square inch. Severely cold-worked iron may show a tensile strength of 150,000 lb. per square inch. The maximum actual stress is again somewhat higher (165,000), but not in so large a ratio as in the case of the hot-rolled iron. Even in the cold-worked iron, rupture still takes place by degrees—that is, by a kind of tearing action—so that the highest of these figures still does not represent the inherent absolute cohesion.

Some very interesting tests of glass have been reported by Griffith.¹ In ordinary fibers of 0.040-in. diameter the material had a tensile strength of about 25,000 lb. per square inch. The tensile strength was found to increase as the diameter of the fibers decreased, and in very fine fibers, carefully prepared, sur-

¹ GRIFFITH, A. A., "The Phenomena of Rupture and Flow in Solids," *Phil. Tran.*, Series A, vol. 221, pp. 163-198.

prisingly high values were obtained. The maximum strength recorded was 492,000 lb. per square inch at a diameter of 0.00012 in. Plotting the reciprocal of the tensile strength against the diameter of the fiber and extrapolating to zero diameter, Griffith found a value of 1,600,000 lb. per square inch, representing the theoretical "absolute cohesion" of the glass.

Calculations based on the energy required to separate the atoms of metals by vaporization give values up to about 5,000,000 lb. per square inch for the "intrinsic pressure," a quantity which is theoretically of the same order of magnitude as the absolute cohesion.

The accuracy of Griffith's extrapolation and of values for cohesion derived from the heat of vaporization may be questioned. The actual numerical values reached are of little significance. The important thing is that metals possess very great inherent cohesion, greater probably than is ever realized in tensile tests of the pure metals or their strongest alloys. Looked at from this point of view, the problem of the hardening and strengthening of metals by various means becomes more simple. Instead of inquiring why metals are so strong, it may better be asked why metals are so weak.

Hardening Due to Slip Interference.—Metals are crystalline and are built up of atoms arranged in definite and repeating patterns. The regularity of atomic arrangement gives rise to certain planes of weakness, or low resistance to shearing stress. When an external load produces a shearing stress on such a plane, which exceeds the resistance of the crystal to shear on that particular plane, fracture of the crystal takes place. The fragments formed may or may not adhere to each other. If they do not, the failure of the crystal is complete, and it is said to be brittle. The plane of weakness is then known as a "cleavage plane." More generally, in the useful metals, the crystal fragments adhere and merely glide or "slip" over each other. The result of such slip, repeated on many planes, is a measurable permanent deformation. The crystal is ductile, and the planes of weakness are called "slip planes."

The first appreciable formation of slip planes marks the beginning of plastic deformation and, therefore, the passing of the elastic limit. The resistance to permanent deformation, which is a general measure of hardness and strength, represents resistance to the beginning and propagation of slip. Anything that

serves to hinder slip is a source of strength and hardness. *The hardening and strengthening of metals by any of the known methods may be considered as due principally to interference with slip.*

Hardening Effect of Grain Refinement.—In an aggregate of many grains of different orientation, there cannot be any continuous plane of weakness. The application of a load cannot produce any slip planes extending entirely across the section, as in the case of a single grain. When slip takes place in any one grain it cannot continue without change of direction into adjacent grains, because, except in very rare instances, the potential slip planes of adjacent grains do not register. The permanent deformation of the metal is thus resisted at the grain boundaries by the disregistry of the planes of low cohesion, and, especially in fine-grained metals, by the specific hardness of the amorphous cement, which hardness itself is due to the absence of planes of weakness. The result is an increase in elastic limit, hardness, and strength.

Hardening by Cold Work.—Permanent deformation of a metal below the recrystallization temperature involves the breaking up of the grains into fragments along intersecting systems of slip planes and movement of these fragments with respect to one another. Cold work produces a structure unlike that obtainable in any other way. The movement at slip planes is now known to be, in part, one of rotation, so that changes of orientation from grain fragment to grain fragment are or may be produced. In so far as new orientations are created, the effect of cold work is somewhat similar to grain refinement. This is believed to be the chief cause of work-hardness.

The original grain boundaries persist even after severe cold working, and the mechanism of deformation is such that change of orientation of grain fragments near the old grain boundaries should be more pronounced than in the interior of the grain. It is also probable that amorphous metal exists at the grain boundaries. The original grain boundaries, therefore, offer considerable resistance to slip. Since some of the slip surfaces develop greater strength than that required to produce shear on a potential slip plane of a crystal fragment, such surfaces add to the hardness of worked metals.

Although moderate cold work tends to produce mixed orientations of the crystal fragments within any given grain, severe cold working tends to orient the crystal fragments of *all original grains*

in certain definite directions with reference to the direction of working.

The causes of work hardness may be summed up as follows:

1. Cold work produces a structure which simulates in many respects that of a very fine-grained metal.

2. Because of the manner of origin of the cold-worked structure, each grain fragment may have an orientation only slightly different from that of its neighbors, so that a large number of grain fragments may be so oriented as to be traversed by a single slip. Slip through such grain fragments is, however, interfered with by the disregistry at the fragment boundaries, and therefore the hardness is increased. In other words, the main cause of strain hardening is the slip interference resulting from the disregistry of slip planes at the boundaries of grain fragments.

3. An additional cause of strain hardening is the disorganized layer of atoms at self-stopping slip planes and the additional amorphous metal generated at the old grain boundaries.

4. Since severe cold work tends to produce uniformity of orientation among the grain fragments, it is probable that there is a limit to the hardness attainable by cold work. Judging from the hardness of severely cold-worked iron and severely cold-worked aluminum, the maximum hardness attainable by cold work is much lower than that attainable by other methods, such as alloying and heat treating, and hence much lower than the hardness corresponding to the absolute cohesion of the metal.

Nature of Solid Solutions.—It is a general rule that metals are hardened and strengthened by the addition of elements which dissolve in them to form solid solutions. Present knowledge of the structure of solid solutions is quite limited, but from the results so far obtained it seems that the atoms of the solute usually replace those of the solvent in the space lattice of the latter, up to the limit of the first or Alpha solution, in case of limited solubility, or the first of a series of solid solutions. This conclusion is based upon studies of alloy series in which the components have similar atomic volumes, and somewhat different conditions may obtain when this criterion is violated, for example, in the case of iron and carbon. There is good reason to believe, however, that in all cases solid solutions are characterized by the atomic dispersion of their components.

Condition of Compounds in Solution.—When an intermetallic compound forms and dissolves in one of the component metals,

it has been commonly considered to go into solution "as such." For example, carbon has been generally held to be in solution in Gamma iron as iron carbide rather than as elementary carbon. This implies that distinct molecules of iron carbide are dispersed in the Gamma iron.

From the evidence available, and particularly from a consideration of the phenomena of diffusion, the authors have reached the conclusion that this is not the case, but that the carbon in austenite is present as individual atoms of carbon. These atoms are undoubtedly held strongly to the neighboring iron atoms, but the union is not permanent. Diffusion must consist in a migration of carbon atoms, and not of groups or "molecules" containing several iron atoms. Such groups could not, on account of their size, diffuse through solid iron.

According to this view, cementite has no existence except as a crystalline substance, which is not merely precipitated but *formed* on the decomposition of austenite.

Hardness of Solid Solutions.—The increased hardness and strength of solid solutions are traceable directly to increased interatomic forces, the attraction between unlike atoms being, in general, greater than between like atoms. An additional mechanical factor may be conceived, in the form of a roughening of the slip planes, due to the presence of atoms of unlike size, or, as Bridgman puts it, a staggered arrangement of the atoms. The hardening and strengthening effects of grain refinement and cold working apply to solid solutions as well as to pure metals, and are superimposed upon the hardening effect of the solute.

Metallic Compounds.—The structural constituents in alloys which possess the greatest specific hardness and strength are the intermetallic compounds and non-metallic compounds, such as oxides. In general, these compounds are of a low order of symmetry, which, together with the large interatomic forces involved, accounts for their great hardness. The atoms are probably arranged in such a way that those of one element are not interchangeable with those of another element. This fact would account for their lack of plasticity.

One of the most important factors in the loading of any brittle material is eccentrically distributed stress. A ductile material subjected to eccentric loading quickly adjusts itself by permanent deformation at points where the stress exceeds the elastic limit, with comparatively little damage. This is not possible in a

brittle substance and, if the stress at any point in a piece subjected to load exceeds the elastic limit, rupture results. It is obviously easier to avoid local overstressing in small pieces than in large pieces. This accounts for the fact that many materials, which are commonly thought of as very fragile, show remarkably high strength when tested in small sections. Vitreous silica, for example, is quite easily broken when in fairly large pieces, although it shows a tensile strength as high as 160,000 lb. per square inch in the form of fibers. The great strength of glass has already been referred to.

This point is important in the present discussion in connection with intermetallic compounds. These substances are, as a rule, hard and brittle, and are too commonly considered to be weak. Their true strength, when properly protected against eccentric loading by their small size and by embedding in a ductile matrix, is undoubtedly very high. It may safely be assumed that cementite, for example, has a strength of several hundred thousand pounds per square inch.

The Obstruction Principle.—It has long been recognized that the presence of a hard and strong constituent in an alloy may strengthen it by opposing "flow," or slip, in the weaker constituent. Just as slip is opposed at the grain boundaries of a pure metal by the change in orientation, it may be opposed to a still greater extent if the material at the grain boundary possesses, in addition to its different orientation, a specifically greater hardness. The most familiar example of this is the reinforcing effect of the pearlite constituent in hypo-eutectoid steels. While pearlite is not a homogeneous constituent, it may well be imagined to have an effect like that exerted by hypothetical similar grains of a strong solid solution. The structurally free ferrite is the continuous phase, in which the pearlite is scattered as disconnected islands. If the free ferrite were a structureless amorphous substance, the pearlite could produce only a mild strengthening effect, by a sort of frictional resistance to flow, but the ferrite is crystalline and yields only by slipping on its crystallographic planes of weakness, and such slip is opposed by the rigidity of the pearlite.

This mechanism of hardening, which has been described as the "obstruction principle,"¹ refers particularly to reinforcement of a continuous ductile matrix by grains of a stronger constituent,

¹ HOWE, HENRY M., "The Metallography of Steel and Cast Iron."

which are similar in size to the grains of the matrix. The grains of the matrix are strengthened by *external* support.

Hardening by Particles within Grains.—Metals can be hardened to a still greater degree by a hard substance in the form of small particles dispersed *within* the grains. A steel containing 0.90 per cent carbon in the form of small, round particles of cementite having an average diameter on the order of 0.0001 in. has a Brinell hardness of about 160 as compared with a hardness of about 80 for the ferrite matrix when free from carbon.

The ability of disconnected particles of a hard substance to harden a matrix is dependent on the crystalline structure of that matrix. The ferrite matrix in the steel just mentioned is soft because of the presence of many planes of weakness. The cementite particles scattered through this matrix harden it by interfering with slip along these planes. The particles may be considered to act as *keys* mechanically obstructing motion along the planes of weakness. The result is increased elastic limit, hardness, and strength.

The hardening effect of a given amount of hard material thus dispersed within the grains of a ductile crystalline matrix is very largely dependent on the size of the particles. Troostite consists of particles of cementite of submicroscopic size dispersed in ferrite. A steel containing 0.90 per cent carbon in the troostitic condition has a Brinell hardness around 400 or 500. This greatly increased hardness, as compared to granular pearlite, is due partly to the much smaller size of the cementite particles and partly to the smaller size of the grains of the ferrite matrix.

The effect of particle size is masked in the case of steel by accompanying changes in the grain size of the matrix. The principles are shown more clearly in certain aluminum alloys, in which the size of the hard dispersed particles can be varied through a wide range without any change in the grain size of the matrix. From a study of these alloys, it appears that the hardness increases as the particle size decreases, but that a particle size is finally reached which produces maximum hardness. Smaller particles have somewhat less hardening effect.

The average size of particle which produces maximum hardness has been referred to as the *critical* size, and the hard substance is said to be in a condition of *critical dispersion*.

Requirements of Hard Particles.—An impression has been prevalent that the well-known hardening effects of certain dis-

persed substances, like cementite in steel, are largely dependent on the surface forces between the dispersed particles and the matrix, and that the dispersed substance must possess some degree of adhesion or affinity for the substance of the matrix. According to this view, effective hardening could only be expected from those metallic constituents like Fe_3C and CuAl_2 , which are normal alloy constituents, and would not be expected from non-metallic substances like oxides, which are ordinarily present in alloys by mechanical inclusion. The explanation given above, based on the principle of slip interference, indicates that any substance properly dispersed in a ductile crystalline matrix will produce hardening, provided the dispersed substance is harder than the matrix, and that the dispersed substance need not possess a high degree of adhesion for the matrix. Considerable hardening effects are produced in copper by copper oxide, and even by thoria in tungsten.

It is not to be expected that a soft substance dispersed in a harder matrix will harden that matrix. It would not, for example, be expected that dispersed particles of lead would harden copper. It has been reported, however, that Beta brass can be hardened by the presence of dispersed particles of the Alpha phase, which by itself is softer than the Beta phase. A moment's consideration shows this to be quite natural, since the probabilities are very great that the orientations of the small Alpha particles will seldom correspond to the orientations of the Beta grains in which they are embedded. For this purpose, a dispersed substance may be considered harder than its matrix when its shearing strength, in a random direction, is greater than that of the matrix along its planes of easiest slip.

Summary.—1. The absolute cohesion of pure metals is far in excess of values obtained for tensile strength. It is in most cases entirely sufficient to account for the maximum hardness of the alloys of the metals.

2. Mechanical failure under stress is ordinarily premature because of the presence of crystallographic planes of weakness or potential slip planes. These planes permit sliding of one crystal fragment on another at loads much lower than that represented by the absolute cohesion. This slip mechanism allows rupture of atomic bonds by degrees, which accounts for the observed softness of pure metals, notwithstanding the high absolute cohesion.

3. Any structural condition which interferes with slip on these planes of weakness increases the strength and hardness of the metal. Furthermore, every known method of hardening metals can be referred to this principle of slip interference.

4. In a pure metal the most simple source of increased hardness is grain refinement, which introduces slip interference at the grain boundaries due to the different orientations of the adjacent grains, and, especially in fine-grained metals, to the disorganized or amorphous metal between the grains.

5. Cold working introduces slip interference by change of orientation of the small grain fragments between intersecting slip planes and, to a lesser extent, by the disorganization of atomic arrangement at slip planes and at original grain boundaries.

6. The hardness and strength of amorphous metal itself are due to the absence of the planes of weakness characteristic of crystals.

7. Solid solutions are harder than the pure solvent metals, because slip is interfered with by the greater attraction between unlike than between like atoms, and by the roughening of slip planes due to solute atoms of different effective size than the solvent atoms.

8. Intermetallic compounds are hard and brittle because of the high attractive forces between the combining atoms, the non-interchangeability of positions of unlike atoms in the space lattice, and the low crystalline symmetry of the space lattice.

9. The presence in an aggregate of any constituent having high specific hardness interferes with slip in the surrounding material and thereby increases the hardness of the aggregate.

10. Slip within grains is opposed by the presence of a strong constituent at the grain boundary, provided that, if the strong constituent is brittle, its shape and size are not such as to lead to effective weakness, due to eccentricity of loading.

11. Effective hardening is obtained by slip interference within the grains, due to the presence of hard constituents in the form of very fine particles.

12. It is not necessary that the hard constituent possess great adhesion for the matrix.

13. The effect of a given amount of hard constituent increases with the fineness of subdivision, reaching a maximum at an average particle size denoted by the term "critical dispersion."

The critical dispersion probably consists of the smallest particles having the characteristic properties of the crystalline substance. The order of magnitude of the diameter of such particles is probably about 10^{-7} in. A higher degree of dispersion, particularly the atomic dispersion of solid solutions, is less conducive to hardness.

14. Corresponding to the maximum hardness at critical dispersion, there is a minimum in plasticity.

15. Increase in the amount of dispersed substance produces increased hardness, but the brittleness also increases, so that there is a limit to the useful hardness and strength that can be obtained.

16. The amount of hard dispersed substance which produces the greatest useful strength increases as the size of particle increases.

17. The actual amounts of hard dispersed substances which produce useful hardening results are from about 1 to 20 per cent by volume.

18. The manner in which the highest degrees of dispersion are produced consists in the limited decomposition of solutions and, in particular, of solid solutions.

CHAPTER XII

THE HARDENING OF STEEL

It is the purpose of this chapter to summarize the evidence bearing on the nature of hardened steel and to present the views of the authors regarding the causes of hardness in the light of all evidence available up to date. As a preliminary to the discussion of steel, see the statement of the general theory of hardness given in Chap. XI.

Grain Refinement in Pure Iron at A_3 Point.—When pure iron is heated above 900°C . ($1,652^\circ\text{F}$.) so as to cause the A_3 allotropic change to take place, a complete change in its crystalline structure occurs. The body-centered cubic lattice of the Alpha iron changes to the face-centered cubic lattice of Gamma iron. There is a contraction of volume on the order of 1.5 per cent when Alpha iron changes to Gamma iron. The grains of Gamma iron form from many centers or nuclei, which are usually at the grain boundaries of the Alpha iron. The grain boundaries of the Gamma iron do not coincide with old grain boundaries of the Alpha iron. In other words, the transformation of Alpha to Gamma iron not only represents a change in space lattice, but also the entire disappearance of the Alpha grains and the birth of new Gamma iron grains, whose size and shape are determined by the ordinary conditions affecting grain growth. The A_3 transformation point is in a temperature range of grain growth for both Alpha and Gamma iron.

When Gamma iron is cooled through the A_3 point so as to form Alpha iron, an entirely new set of Alpha iron grains is formed. The formation of Alpha iron involves an expansion of the same magnitude as the contraction when Alpha changes to Gamma iron. The new Alpha grains begin to form at the grain boundaries of the Gamma iron. The size and shape of the new Alpha grains will depend largely on the conditions obtaining during and after the transformation. \ Slow cooling allows time for growth of the Alpha grains and favors the formation of relatively few nuclei. Rapid cooling, as, for example, water-quenching from above A_3 ,

promotes the formation of more nuclei and retards grain growth after the transformation is complete.¹)

Pure Iron Not Hardened by Quenching.—Samples of Armco iron containing about 0.02 per cent carbon showed about seven times as many grains per unit volume when quenched from 1,300° C. (2,372° F.) as when furnace cooled from the same temperature. This reduction in grain size is slight and the change in properties between quenched and furnace-cooled Armco iron is correspondingly small. It does not seem possible to affect the grain size of pure iron greatly by quenching through the A_3 transformation point. Pure iron has been referred to, therefore, as incapable of being hardened by quenching from above the so-called upper critical temperature, which is the A_3 point. It is probable that the lowering of the transformation temperature of Gamma iron to Alpha iron at A_3 by quenching is very slight. The heat evolved and the relatively high temperature of the transformation, coupled with the low thermal conductivity of iron, seem to allow pure iron during quenching sufficient time in which to form relatively large grains of Alpha iron.

Hardening of Iron-nickel Alloys by Quenching.—When pure nickel is added to pure iron, the A_3 transformation of the alloy is progressively lowered from about 900° C. (1,652° F.) to room temperature, as the nickel content is increased from zero to about 25 per cent. On rapid cooling from a high temperature, samples containing 85 per cent iron and 15 per cent nickel can be obtained at room temperature in the Gamma or austenitic condition. If cooling takes place at such a rate as to allow the Gamma-Alpha change to occur, the grain size of the transformed alloy becomes smaller as the temperature of A_3 is lowered, because the low temperature of transformation produces undercooling, and hence favors the formation of many nuclei and defeats grain growth.

There is very little information regarding the mechanical properties of pure iron-nickel alloys having a nickel content up to 25 per cent. Much work, however, has been done on iron-nickel alloys containing small amounts of carbon. An iron-nickel alloy containing 7.54 per cent nickel, 0.09 per cent carbon, and 0.04 per cent manganese had its strength doubled by quenching from a dull red heat. A steel of the same composition, but with-

¹ JEFFRIES, ZAY, "Grain Size Inheritance in Iron and Carbon Steel," *Trans. Am. Inst. Mining Eng.*, vol. 58, p. 669, 1918.

out nickel, shows very little change in physical properties after quenching.¹ Edwards concludes, from a general review of the work on iron-nickel alloys, that the presence of carbon is not necessary for hardening to take place on quenching.

The hardness of these iron-nickel alloys in the fine-grained condition is partly accounted for by the nickel in solid solution in the iron, but is due chiefly to the marked refinement of grain. When nickel is added to iron, only the A_3 transformation is affected, and this may be lowered to any desired temperature below 900° C. (1,652° F.), and with sufficient nickel the transformation does not take place at all. At the A_3 point in iron-nickel alloys there is only the Gamma to Alpha transformation to take place, and if this takes place at a sufficiently low temperature the Alpha modification will be fine-grained and, consequently, relatively hard and strong.

The Allotropic Transformation in Iron-carbon Alloys.—Likewise, when carbon is added to iron, the A_3 transformation is lowered but, with more than about 0.05 per cent carbon, the transformation is not a simple one, as in the case of iron-nickel alloys, but is composite, yielding under equilibrium conditions two products, ferrite and cementite. It is very probable, as has been pointed out, that the carbon in austenite exists in atomic dispersion. When either Gamma or Alpha iron becomes supersaturated with carbon, the excess precipitates as Fe_3C . Gamma iron is much more capable of holding carbon in solution than is Alpha iron. The line *GS* in Fig. 108 shows how the A_3 transformation of iron is lowered with increase in carbon content. Line *ES*, Fig. 108, represents the temperature-solubility relations of carbon in Gamma iron. The intersection of these two lines, *S*, is the eutectoid point.

Eutectic vs. Eutectoid.—Although a eutectic and eutectoid are similar in many respects, there are some important differences between the eutectic transformation and the eutectoid transformation. These differences are so far-reaching in their effects as to make steel susceptible to marked improvement in hardness by heat treatment, whereas no changes of such magnitude can be brought about by treatment of eutectics. In a liquid binary alloy of eutectic composition, the atoms of both constituents are present in a thoroughly dispersed state and the like atoms must get together during solidification. The molten state is

¹ EDWARDS, C. A., "Physico-Chemical Properties of Steel," p. 164.

one of very great freedom of movement of atoms, which makes it relatively easy for the atoms of each constituent to get together. Both constituents of a binary eutectic must crystallize from a non-crystalline liquid solution. The heat of crystallization is relatively high and solidification cannot take place without a substantial halt, due to the evolved heat of crystallization. Such a halt favors the segregation of the two constituents. Furthermore, the temperature of formation of a eutectic is high, relatively, being the highest temperature, or nearly so, at which the mixture is capable of existing in the solid state. These conditions favor rapid segregation of the atoms required to form the different constituents.

Allotropic Change Easier than Carbide Formation.—In the iron-cementite eutectoid the ferrite is the product of transformation of atoms of iron from one crystalline form to another, a weaker change than that of liquid to crystal. The change involves less energy and is more easily retarded by rapid cooling. The eutectoid, pearlite, can even be heated somewhat above its equilibrium transformation point without changing to austenite, a thing never observed in the change from the crystalline to the liquid state. The other product of the eutectoid transformation, cementite (Fe_3C), cannot form without diffusion of carbon through solid crystalline metal. The change of Gamma iron to Alpha iron involves only minor movements of the iron atoms. Formation of cementite from iron atoms and carbon atoms, the latter being as far apart as they can get in the Gamma iron space lattice, involves diffusion of the carbon. This requires much more time than that required for the transformation of the iron from one space lattice to another. It is not surprising, therefore, that the allotropic transformation from Gamma iron to Alpha iron can be effected without allowing any substantial amount of cementite to form. Furthermore, it is not surprising that rapid cooling of high-carbon austenite suppresses the allotropic transformation to a temperature of 300°C . (572°F .), or less.

The sluggishness of the eutectoid transformation as compared with the eutectic transformation is strikingly illustrated in Fig. 181. This micrograph shows the structure of an iron-carbon alloy (1.6 per cent C.) quenched from a temperature at which it is partly liquid and partly solid (austenite). The liquid portion, represented by the intergranular material in the micrograph, has produced a typical chilled, white cast-iron structure, in which

the presence of cementite is quite evident. That portion of the alloy which was solid austenite at the time of quenching has remained austenite, or been converted to martensite. Free cementite is not visible in the micrograph in the portions which were solid at the time of quenching.

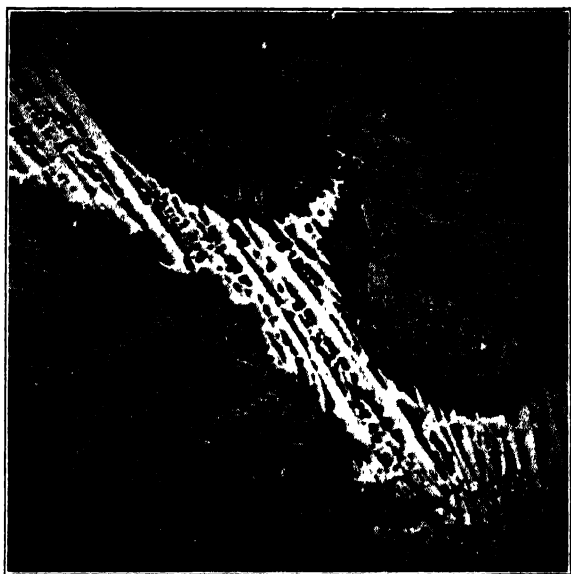


FIG. 181.—1.6 per cent carbon steel quenched above solidus. $\times 1,000$. (Zimmerschied-General Motors.)

Martensite.—When the allotropic transformation of the iron takes place on quenching a carbon steel, without the simultaneous formation of the carbide, the carbon is very likely temporarily trapped in atomic dispersion in the transformed austenite. The product of this quenching, in which the carbide formation is temporarily suppressed, is the constituent of steel called *martensite*.

Martensite has a variable carbon content, being the same as that of the austenite from which it was formed at the moment of the allotropic transformation. Its properties vary with the carbon content and with physical differences, such as those due to different quenching temperatures or maximum temperature of treatment before quenching. Carbon steels containing less than about 0.15 per cent carbon do not form hard martensite when quenched from above the upper critical temperature. Carbon

steels containing about 0.2 per cent carbon form a medium-hard, but ductile, martensite when rapidly quenched from above the upper critical temperature. The hardness increases with the carbon content up to about 0.7 per cent carbon, above which there is a less marked change in hardness up to about 1.5 per cent carbon. The lower the carbon content the more drastic must be the quench in order to produce martensite. For example, the mildest quench which will produce 100 per cent martensite in a 0.9 per cent carbon steel will produce free ferrite, martensite, and



FIG. 182.—Martensite and austenite in bearing steel. $\times 1,000$. (Walp, S. K. F. Research Laboratory.)

troostite (or sorbite) in a 0.2 per cent carbon steel, and martensite and troostite in a 0.5 per cent carbon steel.

Microstructure of Martensite.—Martensite, under the microscope, appears to be devoid of specific structure, except a tendency toward the so-called “acicular” or needle-like markings, having the same angles as the crystallographic planes of the mother austenite grains. The larger the austenite grains from which the martensite is formed, the more pronounced are these markings. The martensite of commerce is usually produced by quenching fine-grained austenite and, consequently, it does not possess the marked acicular structure usually considered as typical. Figure 182 is a bearing steel containing high carbon and some chromium, and quenched from $1,035^{\circ}\text{C}$. ($1,900^{\circ}\text{F}$.).

Coarse-grained austenite existed prior to quenching and the markings are typical of acicular martensite. The conditions in this case were such that some austenite was preserved by the quench.

Retention of Austenite.—The retention of austenite at ordinary temperature is favored by the presence of nickel, as mentioned above, by chromium, by manganese, and by high carbon. Austenite is not nearly as hard as martensite. Transformation of austenite to martensite is, therefore, accompanied by an increase in hardness. Since the face-centered cubic crystal lattice of austenite represents closer packing of the atoms than the body-centered lattice of Alpha iron or martensite, the transformation of austenite to martensite is accompanied by an increase in volume. Those elements which, when present in considerable amounts, are conducive to the retention of austenite on quenching are, when present in small amounts, conducive to the formation of martensite on quenching. These elements can be substituted for part of the carbon in steel, but no element has been found which can entirely replace carbon in iron-base alloys. The alloy steels form martensite on quenching more readily than carbon steels. This difference is very apparent in large sections of steel which form a much thicker hard layer on the surface with alloy steel than with carbon steel.

Pearlite, Sorbite, and Troostite.—The rate of cooling any steel from the critical temperature is a most important factor in determining its structure, and hence its properties. Consider the effect of various rates of cooling a 0.9 per cent carbon steel from the austenitic state. There is only one phase, namely, Gamma iron, in which 0.9 per cent carbon is dissolved (austenite). If cooled very slowly through the critical range, pearlite is formed, in which the cementite tends toward globular particles large enough to be seen under the microscope at, say, 100 to 200 magnifications. Figure 183 is a micrograph of high-carbon steel in which the cementite is globular. With somewhat more rapid cooling, such as the air cooling of a piece of steel about 1 in. on a side, the well-known lamellar pearlite, as shown in Fig. 184, is formed. The more rapid the cooling the smaller the cementite particles become, until a size of particle is reached which is no longer resolvable under the highest powered microscope. In accordance with the etching characteristics of these mixtures of ferrite and fine particles of cementite, they are termed "sorbite"

or "troostite." These constituents in steel are not very well defined, as might be expected, because they do not represent

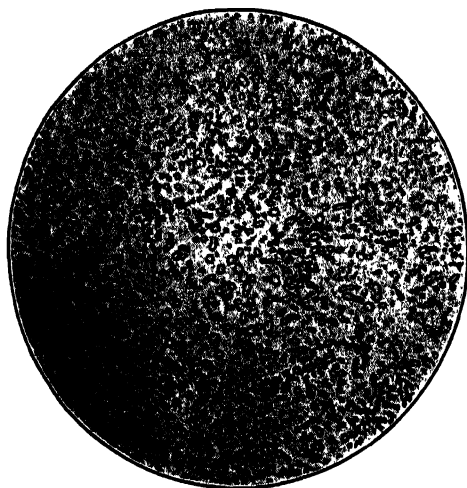


FIG. 183.—Bearing steel in which the cementite is globular. $\times 1,000$. (Walp, S. K. F. Research Laboratory.)

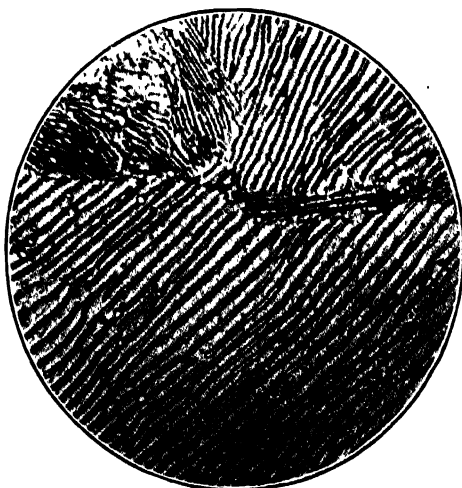


FIG. 184.—Lamellar pearlite. $\times 1,000$. (Walp, S. K. F. Research Laboratory.)

phase differences, but only changes in grain size of the same constituents.

Formation of Martensite.—The temperature of transformation of the austenite becomes lower the more rapid the cooling rate. As the transformation temperature becomes lower, the ferrite grains become smaller and the cementite particles become smaller. The lowering of the temperature of the transformation, however, is not continuous as the rapidity of the cooling increases. When the cooling rate is proper to lower the transformation temperature to about 600° C. (1,112° F.), troostite, consisting of fine-grained ferrite and small particles of cementite, forms. When the cooling rate is sufficient to lower the transformation temperature substantially below 600° C., there seems to be no change in the austenite until a temperature in the neighborhood of 300° C. (572° F.) is reached. At this temperature, or at some lower temperature, the allotropic transformation from Gamma iron to Alpha iron takes place without the formation of cementite. The freshly formed product of such a quench is, therefore, different constitutionally from troostite, sorbite, or pearlite. There seems to be very little difference in the quenching rates required to produce martensite and troostite, as evidenced by the simultaneous occurrence of these two constituents in many quenched steels. The point to be emphasized in this connection is the discontinuity in the lowering of the transformation temperature of austenite with progressively faster cooling rates. If the austenite can be cooled fast enough to reach a temperature below about 600° C. (1,112° F.) without transformation, there seems to be a considerable temperature range within which it is more stable than at about 600° C. or below about 300° C.

Formation of Cementite from Martensite.—As mentioned above, no substantial diffusion of atoms is necessary in the transformation of face-centered iron to the body-centered lattice. Since carbon is very much less soluble in Alpha than in Gamma iron, there is a strong force toward precipitation of carbide as soon as the iron transformation has taken place. In order for cementite to form, however, the carbon atoms must diffuse. Carbon can diffuse slowly at room temperature in the iron lattice and does so, forming cementite. At higher temperatures the reaction takes place more rapidly. The result of the carbide precipitation at low temperatures is decidedly different from that when the carbide forms at or above about 600° C. The cementite forms from more centers at the lower temperatures,

and at some stage of the precipitation the particles must be of critical size to produce maximum hardness.

Freshly formed martensite, therefore, is composed chiefly of Alpha iron holding carbon atoms in atomic dispersion. Martensite which has stood at room temperature for a considerable time, or which has been subjected to elevated temperatures below those at which the martensite may be regarded as having transformed into troostite, consists of ferrite and innumerable small particles of cementite. The ferrite may or may not contain more than the equilibrium quantity of carbon in atomic dispersion, or true solution.

Grain Size of Martensite.—Because of the low temperature at which it is formed and the obstructing effect of the carbon in solution, the grain size of the Alpha iron of which martensite is composed is very small.

Causes of Hardness of Martensite.—After considering all of the evidence, the authors have concluded that the hardness of martensite is due chiefly to the fineness of the ferrite grains. The presence of carbon atomically dispersed in this ferrite to form a forced solid solution also contributes to the hardness of the product, but is a small factor as compared with the grain size. Crystalline cementite is very hard and strong and meets all of the requirements of a good "key" material. The formation of particles of cementite in martensite is, therefore, an additional source of hardness. At some stage in the formation and growth of the cementite particles their size is such as to produce maximum hardening effect. It is not probable that all of the cementite particles reach critical size at the same time.

Growth of Cementite Particles.—After the cementite formation has progressed nearly to completion, the larger particles grow by absorbing carbon in solution in the ferrite. The ferrite is supersaturated in carbon with respect to the larger particles and saturated with respect to smaller particles of cementite. The precipitation of the carbide on the larger particles produces a condition of undersaturation with respect to smaller particles which then are dissolved. The carbon atoms diffuse toward regions of low concentration, which is toward the larger particles. Growth of cementite particles during tempering is thus favored by a long time and high temperature. The successive stages of troostite, sorbite, and granular pearlite represent, in part, progressive increase in size and decrease in number of the cementite particles.

Ferrite Grain Growth.—As these changes in the carbide are progressing, there must be some changes in the ferrite. In the case of a steel containing 1 per cent carbon, the formation of cementite requires about 15 per cent of the iron. This iron must be supplied from the ferrite or from any amorphous iron which may be present. Such a change is toward a more perfect equilibrium in the ferrite which tends toward softening. It seems certain that the growth of the ferrite into larger particles at temperatures from 350 to 550° C. (662 to 1,022° F.) is an important factor in the decrease of hardness. The effect of changes in the ferrite caused by low tempering (below 300° C.) is small, but even this becomes appreciable in the harder martensites.

Opposing Nature of Ferrite Grain Growth and Cementite Precipitation.—The first stages of tempering martensite, therefore, involve two opposing factors: The changes in the ferrite tend to produce softening, while the first precipitation of the cementite tends to harden. An increase or decrease in hardness, according to the rapidity and extent of these opposing changes, might be expected. It does not appear that a hard steel will ever soften at ordinary temperature. This indicates that there is no considerable growth of ferrite at room temperature, even after many years, and the cementite particles do not reach a super-critical size. Long exposure at about 100° C. seems to produce slight softening in very hard martensite.

Summary.—The essential points in connection with the hardening and hardness of steel are as follows:

1. Steel owes its hardness fundamentally to the absolute cohesion of the iron atoms.
2. Pure iron and soft steels are relatively soft and weak, because of the presence of crystallographic planes of weakness or potential slip planes in the iron or ferrite grains.
3. The increased hardness and strength of pearlite, as compared to pure iron, are due largely to the increased resistance to slip in the ferrite grains offered by the hard intermetallic compound, cementite.
4. The increased hardness of sorbite and troostite, as compared to pearlite, is due to the refinement of the ferrite grains and the greater dispersion of the cementite particles.
5. The increased hardness of martensite, as compared to troostite and sorbite, is due to a still greater refinement of the ferrite grains and, in cases of maximum hardness, to the critical

dispersion of the cementite particles. Carbon in solution or in atomic dispersion in the ferrite makes the ferrite of martensite somewhat harder than the ferrite of pure iron.

6. The more rapid the cooling of austenite the lower will be the temperature of its transformation into ferrite and cementite. When the transformation takes place at or above a temperature of about 600°C . ($1,112^{\circ}\text{F}$.), both ferrite and cementite form, yielding pearlite, sorbite, or troostite. If the austenite is preserved at a temperature less than about 600°C ., it seems to be relatively stable until a temperature of about 300°C . is reached on cooling.

7. When the austenite transformation is suppressed to about 300°C . or lower, the allotropic transformation of the iron takes place independently of the carbide formation. Freshly formed martensite, therefore, consists essentially of Alpha iron in which the carbon is substantially atomically dispersed. Freshly formed martensite is apparently not quite as hard as martensite which has stood at room temperature for several days or has been given a mild tempering treatment.

8. Carbon is very much less soluble in Alpha iron than in Gamma iron. The Alpha iron of freshly formed martensite contains the carbon atoms in atomic dispersion. The Alpha iron of freshly formed martensite is, therefore, supersaturated with respect to carbon. Equilibrium is brought about only by the precipitation of the carbon in the form of cementite.

9. Carbon diffuses slowly in Alpha iron at room temperature and diffuses more rapidly as the temperature is increased. The carbide, therefore, precipitates slowly at room temperature and more rapidly with rising temperature.

10. It is postulated that freshly formed martensite is hard chiefly because of the fineness of the ferrite grains but partly because the ferrite containing carbon is harder than pure ferrite.

11. It is postulated that the increase in hardness of freshly quenched martensite on standing at room temperature or after mild tempering is due to the precipitation of cementite, the hard cementite particles "keying" the slip planes of ferrite grains.

12. Heating tends to soften the martensite because it tends to produce growth of the ferrite grains.

13. Heating produces changes in the carbide which tend to harden the steel until critical dispersion of the carbide particles obtains, and further heating tends to soften.

14. Growth of the carbide particles is considered to take place as the result of a slight solubility of carbon in Alpha iron, which is greater the smaller the size of the cementite particles with which the solution is in contact.

15. The mechanism of particle growth is such that the matrix, Alpha iron, should approximately reach its equilibrium content of carbon before the laws of particle growth would begin to apply. This suggests the nearly complete precipitation of the carbide at an early stage of tempering.

16. Sometimes the composition of the steel is such that rapid quenching preserves austenite at room temperature, whereas moderate rates of cooling do not preserve austenite. The transformation of such austenite to martensite or to another product of transformation on aging or tempering results in an increase in hardness. An increase in the hardness of a steel due to this cause is accompanied by an increase in volume.

The conception of the hardening of steel presented above will be more fully discussed in the following, and further evidence will be given supporting certain of the conclusions.

High Absolute Cohesion of Iron Atoms.—That there is high cohesion between iron atoms is apparent from the hardness and strength of cold-worked iron, and from the energy required to separate iron atoms from one another by evaporation. Iron cannot, however, by cold working be made to develop the maximum hardness or strength which it inherently possesses. The extreme condition of cold working occurs in fine wire drawing. Iron drawn to the finest sizes shows a strength about four times that of annealed iron. The fracture always shows marked reduction of area. This indicates movements of considerable extent on slip planes during fracture, and when such slip occurs the absolute cohesion of the atoms is not developed.

In carbon steels, heat treatment is more effective than cold work in developing slip interference. A steel containing somewhat over 0.4 per cent carbon can be hardened and strengthened to a marked degree by quenching. Such a steel has 1 carbon atom to 50 iron atoms. All of the structural evidence indicates that in such a quenched steel the iron atoms are continuous and the carbon atoms are discontinuous. If the iron atoms are continuous, as seems practically certain, then short paths of rupture are numerous in all directions, which would involve only the separation of iron atoms. If, therefore, the absolute cohesion

of the iron were not high, it would not be possible to make steel so hard and strong. Alloying and heat treatment combine to make steel hard, chiefly by making more effective the cohesion bonds between the iron atoms. Pure iron is soft because of the ease of slip on slip planes, and the hardening is due to interference with slip. The specific ways in which slip is interfered with will now be considered.

Hardness of Granular Pearlite, Sorbite, and Troostite.—These constituents represent different degrees of refinement of the ferrite grains and cementite particles, which are coarsest in pearlite and finest in troostite. Pearlite may be more than twice as hard as pure iron and troostite of eutectoid composition may be three times as hard as pearlite. The slip interference in these constituents is due mostly to the keying action of the cementite and to the refinement of the ferrite grains.

There is good agreement as to the nature of pearlite, sorbite, and troostite.

The Nature of Martensite.—Although definite ideas have been proposed regarding the nature of martensite, there has been much contention for 35 years on this point. It is considered desirable, therefore, to review carefully the evidence for the views given earlier in this chapter.

The reasons for believing that the carbon atoms are in atomic dispersion in austenite have been given. According to this view, the only existence of the compound, cementite, is as a crystalline substance. Crystalline Fe_3C is formed directly from iron and carbon atoms and not from molecules of Fe_3C . It is considered by the authors that there is no molecule containing only 3 atoms of iron and 1 of carbon. If the carbon is in atomic dispersion in austenite, then it will remain in atomic dispersion in transformed austenite (martensite) until cementite forms.

There is considerable evidence that, in the transformation of austenite into martensite, the allotropic transformation of the iron takes place and that it takes place before and independently of the cementite formation. This evidence is of a varied nature involving volume changes, changes in magnetic properties, thermal changes, etching characteristics, and x-ray crystal analysis.

Volume Changes.—It is well known that the transformation of Gamma to Alpha iron takes place with increase in volume.

Andrew, Rippon, Miller, and Wragg¹ have shown that the formation of cementite from austenite causes a contraction. When the steel contains about 1.0 per cent carbon this contraction is sufficient to counteract the expansion due to the allotropic transformation of the iron; a 1.0 per cent carbon steel slowly cooled from the austenitic condition will, therefore, undergo no appreciable volume change other than that due to its normal temperature coefficient. When such a steel is quenched so as to form martensite, however, there is an increase in volume comparable to that accompanying the allotropic change. The expansion has been shown by Chapin² to take place at a low temperature, below 300° C. and to occur simultaneously with the reappearance of magnetism and the development of marked hardness.

Brush³ found that freshly quenched steel contracts in volume slowly at ordinary temperatures. It is well known that tempering causes a decrease in volume. Standing at room temperature seems, therefore, to produce changes corresponding to mild tempering.

When austenite is preserved at ordinary temperatures and is caused to change to martensite, there is a volume increase comparable to that due to the allotropic change.

Magnetic Properties.—It is well known that austenite is non-magnetic unless the proportion of nickel or cobalt is substantial. These elements are magnetic when crystallized with face-centered cubic lattices, and can hold considerable iron without losing their magnetic properties. The transformation of non-magnetic austenite into martensite is accompanied by a sharp increase in magnetic susceptibility. Martensite is always quite magnetic, its susceptibility approaching that of pure Alpha iron.

Honda⁴ has observed a magnetic transformation point in cementite at about 215° C. (420° F.), which he called A_0 . Magnetic analysis is capable of detecting cementite in steel containing as little as 0.1 per cent carbon. Freshly quenched eutectoid martensite shows only a suggestion of the A_0 point on

¹ "The Effect of Initial Temperature upon the Physical Properties of Steel, *J. Iron Steel Inst.*, No. 1, p. 527, 1920.

² *Trans. Am. Soc. Steel Treating*, pp. 507-514, Mar., 1922.

³ "Thermal Relations in the Treatment of Steel," *Trans. Am. Inst. Mining Eng.*, Pyrometry Volume, p. 590, 1920.

⁴ "On Magnetic Analysis as a Means of Studying the Structure of Steel," *J. Iron Steel Inst.*, vol. 98, No. 2, p. 375, 1918.

heating but, once the steel has been heated to 300° C. or above for a short time, the point is pronounced, indicating the presence of crystalline cementite. The effect of particle size on the magnetic properties of cementite is not known, so, from the magnetic evidence alone, it is not safe to draw definite conclusions as to its absence.

Thermal Changes.—Portevin and Garvin¹ have studied the quenching of steel by means of cooling curves. They report that martensite forms at or below about 300° C. on quenching. When the transformation takes place at these low temperatures, not all of the heat of the A₃₂₁ transformation is evolved. This

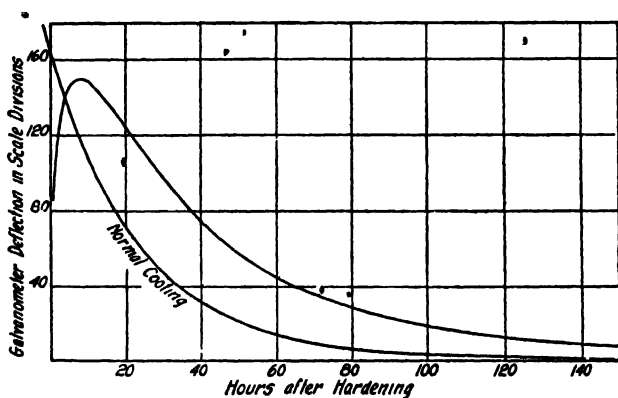


FIG. 185.—Curve showing spontaneous generation of heat in recently hardened steel. (Brush.)

point has been studied quantitatively by Honda² and Yamada,³ who find that a considerable portion of the heat is quickly evolved on reheating the quenched steel to a temperature slightly below 400° C. (752° F.). The amount of heat evolved on reheating was found to be proportional to the carbon content of the steel. In certain steels it was equivalent to about one-third of the heat evolved at A₃₂₁ on slow cooling.

It has long been known that heat was evolved on tempering martensite. C. F. Brush, however, observed the same phenomenon at ordinary temperature. He constructed a very sensitive calorimeter into which he put quenched steel within an hour

¹ *J. Iron Steel Inst.*, No. 1, p. 469, 1919.

² *Chem. Met. Eng.*, pp. 1001–1003, Nov. 30, 1921.

³ *Sci. Reps. Tohoku Imp. Univ.*, vol. 10, p. 453.

after quenching. The evolution of heat from the steel was sufficient to increase its temperature more than 2°C . The heat evolution seemed to be most rapid at first and to lessen gradually. The evolution of heat was sufficient to be detected, however, after 35 days. Brush's graphs showing the spontaneous generation of heat and spontaneous contraction of recently hardened steel are shown in Figs. 185 and 186. The contraction and the heat evolution, at room temperature and on tempering, are attributed by the present authors to the formation of cementite

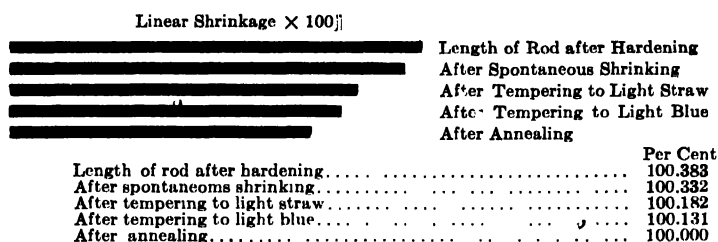


FIG. 186.—Shrinkage of steel bar due to heat treatment. (*Brush*.)

Etching Characteristics.—There is a marked difference between the etching characteristics of martensite and troostite and between martensite and austenite. Martensite is more resistant to acid attack than troostite but less resistant than austenite. From experience with various alloys it seems that the following generalities can be made. When a second phase crystallizes from a solid solution, the corrosive attack becomes only slightly more pronounced if the particle size of the new phase is very small, say smaller than critical size for maximum hardness. When the particle size becomes super-critical, the corrosive attack becomes more rapid.

The behavior of martensite is in keeping with these views. The cementite in untempered or mildly tempered martensite is present as very small particles. In troostite the cementite particles are super-critical in size and the etching or corrosive attack is more pronounced.

X-ray Crystal Analysis.—The x -ray gives a positive answer on the matter of allotropic changes on quenching. When austenite is preserved at ordinary temperatures, the x -ray shows that the crystal lattice is face-centered cubic or that of Gamma iron. When martensite is formed, the crystal lattice is body-centered

cubic or that of Alpha iron.¹ Beta iron has the same crystal lattice as Alpha iron. Since change in crystalline structure is regarded as essential in a true allotropic change, the so-called Beta iron will be treated as Alpha. There is certainly no justification for assuming a Beta iron of such hardness that its supposed retention by quenching accounts for the hardness of martensite.

When austenite is preserved at ordinary temperatures and is later transformed into martensite, the change in crystal lattice occurs simultaneously with increase in hardness, volume, and magnetic susceptibility. The x-ray thus has given a definite and final answer as to the nature of the iron in martensite. It is the ordinary Alpha iron, usually regarded as soft and weak.

The x-ray so far has not given any evidence as to the existence or non-existence of cementite in freshly formed martensite. The authors believe, however, that the evidence given above is quite conclusive on this point.

It should be mentioned that martensite can be formed by rapidly cooling a steel from above the critical temperature to about 200° C. Chapin formed martensite in this manner. Obviously, cementite will form more rapidly at 200° C. than at room temperature. Within a few minutes after the martensite is formed there should be as much cementite formed as after several weeks at room temperature. That this is the case is indicated by the fact that the volume increase is slightly smaller when martensite is formed at 200° C. than when the steel is cooled quickly to room temperature.

Hardness Changes on Tempering.—Too little is known regarding the exact sequence of hardness changes on tempering quenched carbon steels. The most marked effect is one of softening, and the opinion is fairly general that softening is progressive throughout the whole range of tempering temperatures. It is certain that the tempering of hardened tool steel at temperatures above 200° C. reduces its cutting hardness and probably also its Brinell hardness. The Shore scleroscope hardness of tool steel seems to be less affected by tempering at low temperatures. It is likewise quite certain that steels of medium-carbon content, which have been hardened, are softened by tempering at temperatures above 350° C., as proved by thousands of tests on hardness

¹ WESTGREN, "Roentgen Spectrographic Investigations of Iron and Steel," *J. Iron Steel Inst.*, vol. 103, p. 303, 1921; BAIN, "Studies of Crystal Structure With X-rays," *Chem. Met. Eng.*, p. 663, Oct. 5, 1921.

and tensile strength. The hardness of low-carbon steels is known to be not greatly changed by tempering, and the changes brought about by tempering above 500°C . are certainly in the direction of softening. Steels of the various carbon contents are seldom tempered commercially at temperatures below those which produce easily measurable softening. There is, therefore, a lack of results of commercial practice in the tempering of hardened steels at very low temperatures.

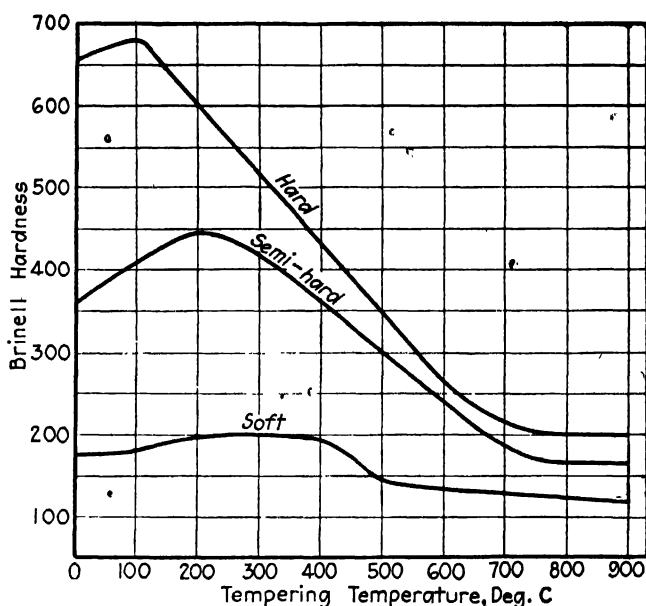


FIG. 187.—Effect of tempering on the hardness of hardened steel. (Grard.)

It is stated by Heyn and again by Boynton that tempering, even in its early stages, gradually reduces the hardness of martensite. Heyn's conclusions are drawn from scratch hardness tests on high-carbon steel.

Among the few published contributions on this subject is a paper by C. Grard, in which it is reported that the first effect of tempering is to increase the hardness. His results are plotted in Fig. 187. They are described as typical of the steels of the classes named. No analyses are given.

While Grard's curves are opposed to general opinion, it is believed that they merit serious consideration as representing

perhaps an overlooked phenomenon in the tempering of steel. He appears to have made a particular point of the accuracy of his hardness determinations. These were also confirmed, in the case of the soft and semi-hard steels, by tensile strength results which parallel the hardness results closely; hard steels were too brittle for satisfactory tensile tests after low tempering temperatures. It is to be noted that the maximum hardness attained on tempering occurs at a lower temperature the higher the initial hardness. Marked softening also begins at lower temperatures the higher the initial hardness.

Honda and Idei¹ have made extensive studies of the hardness of recently quenched carbon steels. Their general conclusions with reference to the distribution of hardness with various rates of cooling are given in their own words as follows:

In small pieces of steel, such as a square or a short cylinder, the periphery is harder than the central portion only when the quenching is very soft. In a moderate quenching the hardness is everywhere nearly equal; but in a hard (drastic) quenching the periphery is always softer than the interior. This anomalous phenomenon is explained by the presence of the arrested austenite.

These authors give, as the chief evidence of the retention of austenite in the hard quenchings, the increase in hardness of hard-quenched steels with considerable lapse of time at ordinary temperatures and more quickly at 100° C. They state:

According to the above view, in a hard-quenched steel, some austenite remains untransformed at room temperature, at which this austenite will slowly transform into martensite. On the other hand, at room temperature, martensite has a tendency further to be transformed into troostite, but the velocity of this change is much smaller than that of the austenite→martensite change just referred to. The consequence is that at room temperature a hard-quenched specimen will slowly increase in hardness with lapse of time. To test this inference, the hardness of a quenched specimen was measured from time to time, as in the usual way, and its mean value plotted against the time passed after the quenching. Figure 188 is a graphical representation of the result of our experiments, which agree completely with our expectation. The hardness increases at first rapidly and then slowly, tending to an asymptotic value as the time elapses.

If the quenched specimen is constantly heated at 100° C., instead of letting it remain at room temperature, the above change from austenite

¹ "On the Distribution of Hardness in Quenched Carbon Steels and Quenching Cracks," *Sci. Repts. Tôhoku Imp. Univ.*, vol. 9, No. 6, 1920.

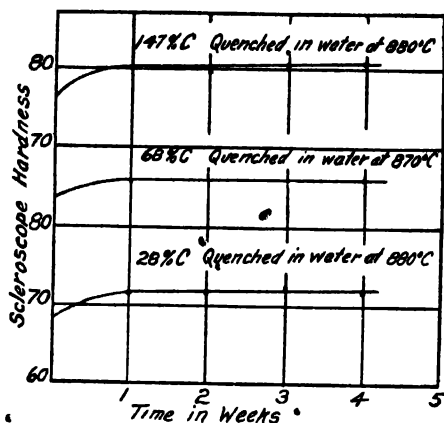


FIG. 188.—Effect of room temperature aging on the hardness of quenched steel. (Honda and Idei.)

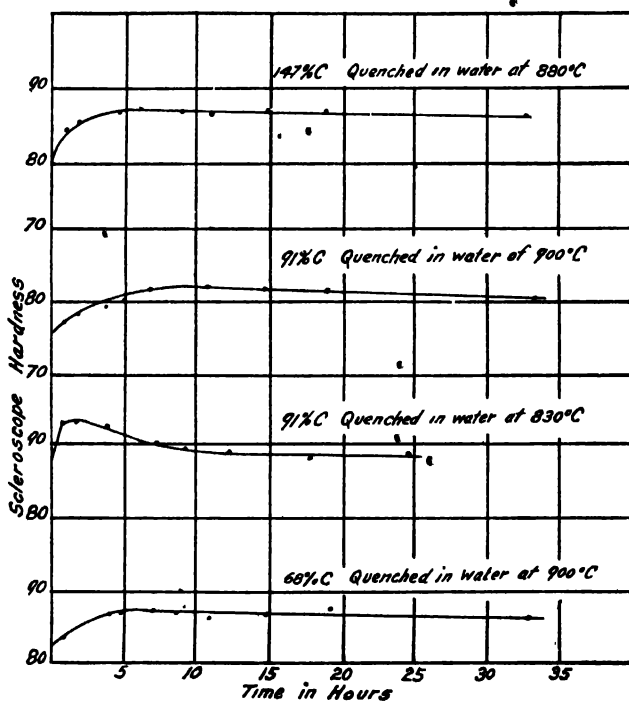


FIG. 189.—Effect of tempering at 100° C. on the hardness of quenched steel. (Honda and Idei.)

will be much accelerated; at the same time the change from martensite to troostite will also be accelerated. Hence the hardness must at first increase, reach a maximum, and then slowly decrease. As shown in Fig. 189, this conclusion is actually brought out by experiments.

Although austenite is retained at ordinary temperature on quenching certain steels, and causes an increase in hardness when and if it transforms to martensite, its retention in ordinary carbon steels, as postulated by Honda and Idei, seems highly improbable. When austenite is retained in any substantial amount, its presence can be detected by *x*-ray analysis. The *x*-ray gives no indication of the retention of austenite in steels similar to those used by Honda and Idei. When austenite transforms into martensite, it does so with increase in hardness and volume and with evolution of heat. Brush found that recently quenched carbon steel evolves heat spontaneously, but the heat evolution is accompanied by a *decrease* in volume. Unless Honda and Idei can show an increase in volume accompanying the increase in hardness, it is almost certain that the hardness increase is due to some change other than the transformation of austenite to martensite.

The explanation put forward in the earlier part of this chapter conforms to all of the observed facts. The spontaneous hardening, evolution of heat, and contraction are due to the precipitation of cementite. In a hard quenching the outside layers of the steel cool to ordinary temperature so rapidly that practically no cementite has formed. Maximum hardness does not obtain until cementite particles form. The formation of cementite takes place slowly at room temperature and more rapidly as the temperature is increased. The rate of cementite formation is governed largely by the rate of diffusion of carbon in the Alpha iron lattice. There is no indication that the transformation of austenite to martensite takes place so gradually. This transformation is usually quite sudden when conditions are proper. This accords nicely with the curves in Figs. 188 and 189.

With a medium quench, the steel remains a sufficient time below about 300° C. and above room temperature to cause precipitation of considerable cementite. If the quench is too soft, troostite may form or cementite particles of super-critical size may form from the martensite.

Frequently large pieces of quenched steel will not be cracked immediately after quenching but will crack within a few minutes,

hours, or days. Such cracking would not be expected to take place if the views of Honda and Idei are correct. They would postulate the existence of martensite and troostite in the interior and martensite containing some untransformed austenite in the outer layers. The slow transformation of the austenite should produce an increase in volume in the outer layers, and hence reduce the tensile stresses. This should prevent cracking. On the other hand, if cementite precipitation occurs in the outer layer, contraction would take place with increase in the tensile stresses. This would promote cracking. It is thus evident that the results of Honda and Idei can be more satisfactorily explained by the spontaneous precipitation of cementite from recently formed martensite than by the transformation of austenite to martensite.

Evidence that Martensite is Fine-grained.—It was postulated that the ferrite of martensite is fine-grained and that the hardness of martensite is due, in large measure, to the fine-grained structure. To account for the great hardness of martensite on this basis, it must be considered that the grain size in martensite is very minute, in fact submicroscopic. There is no direct quantitative method of measuring the grain size in martensite, but there is indirect evidence which shows that it is very small.

It should perhaps be explained what is meant by the grain size of martensite. Martensite is a decomposition product of austenite. The martensitic structure formed by quenching austenite shows many traces of the original austenite grain size. Fracture commonly follows the grain boundaries of the parent austenite. Certain methods of etching frequently reveal these pseudo grain boundaries, at the same time failing to reveal any clear structure within them. It may, therefore, appear that these are the true grain boundaries in the martensitic structures.

These pseudo-grains are, in reality, made up of a large number of differently oriented grains of Alpha iron. It is these grains whose small size is held to be responsible for the hardness of martensite, and it is this grain size to which the following discussion refers.

The conditions governing grain growth in metals under various circumstances have been worked out and it can be said with considerable assurance of certainty that the conditions obtaining during the formation of martensite are such that the grain size of the Alpha iron in martensite must be very small.

While it is impossible to observe the grains in martensite directly with the microscope, it can be inferred from microscopic

examination of other structures that the grains in martensite are too small to be seen. .

The x-ray spectrometer gives evidence of a direct but qualitative nature that the grain size in martensite is very small.

Nucleus Formation in Martensite.—The temperature at which martensite is formed in carbon steel is about 300° C. or lower. This is at least 400° C. lower than the temperature at which Alpha iron forms from austenite under equilibrium conditions. Such undercooling is known in many instances to cause the formation of a very large number of nuclei of the new phase. For example, if water slightly undercooled below the normal freezing point is agitated, there immediately forms a slush much resembling a mixture of fine snow and water. If such a slush is frozen, it is found to be fine-grained as compared to ice formed by normal freezing. Similarly, if ordinary glass which is amorphous is heated so as to cause devitrification, the crystals formed are smaller and more numerous the lower the temperature. The number of Alpha iron nuclei which form in austenite must be greater as the amount of undercooling increases.

Grain Growth.—It is well known that the rate of grain growth in metals increases with temperature and that normally the extent to which grain growth proceeds also increases with temperature. In many metals it seems that there is a fairly definite equilibrium grain size which is more or less stable at each temperature of annealing. Severely cold-worked iron shows visible recrystallization on heating to about 450° C. There seems to be some submicroscopic grain growth at temperatures below 300° C., but it takes place slowly and is very limited in extent. Martensite is formed at a temperature of 300° C. or lower, where any grain growth occurring in Alpha iron must be very small, and must require considerable time.

Obstructing Effect of Carbon.—Grain growth in metals is hindered and sometimes entirely prevented mechanically by the presence of obstructing material as described in Chap. V. The presence of carbon in austenite at the time of its transformation must oppose the growth of the ferrite grains which form. Its presence would impede grain growth both during and after the transformation.

It may be considered that the presence in austenite of carbon atoms in substantially uniform distribution divides the iron atoms into groups. The smaller these groups, that is, the

greater the carbon content, the more stable is the Gamma iron lattice as shown by the lower equilibrium temperature of the transformation. When the carbon content exceeds about 1.5 per cent, the stability of the structure is so great that some austenite may be preserved at room temperature by quenching from above the upper critical temperature. It would seem that the existence of these repeating groups of iron atoms would be conducive to the formation of many Alpha iron nuclei.

Evidence of the Microscope.—Microscopic examination of martensite reveals no Alpha iron unit that could be classed as a grain, yet the *x*-ray spectrometer shows beyond a doubt that martensite is chiefly crystalline Alpha iron. This suggests that the crystalline units are submicroscopic, that is, less than about one one hundred-thousandth of an inch in diameter.

When pure Gamma iron is quenched, the Alpha iron grains are smaller than are produced by slow cooling. As carbon is added to the Gamma iron, the Alpha iron grains not only become smaller on slow cooling, but the effect of cooling rate on the grain size becomes much more marked than with pure Gamma iron. In a hard-quenched, 0.2 per cent carbon steel, the ferrite may be so fine that it is not discernible as individual grains, under the microscope. The inference is that a greater carbon content would cause the formation of still smaller ferrite particles with hard quenching.

All of the refinement of grain at the time of the transformation of Gamma to Alpha iron would be expected. After the Alpha iron has been formed, any change in its structure should be toward greater stability, which is toward larger grains. Tempering martensite at 400° C. to form troostite could not, therefore, represent a change toward greater refinement of grain than existed in the martensite; the change must be in the other direction. Yet in troostite so formed, there is no indication of the presence of grains of ferrite large enough to be seen with the highest powered microscope. Again, the inference is irresistible that the grains of Alpha iron in martensite are submicroscopic.

Evidence of the X-ray Spectrometer.—In order to obtain a good Hull pattern with the *x*-ray spectrometer, it is necessary that the specimen be fine-grained. In a 0.35 per cent carbon martensite, formed by quenching from 1,300° C. (2,372° F.), the Alpha iron pattern was typical of that obtained from fine-grained metals, even though the austenite grains from which

the martensite was formed were large enough to be seen with the unaided eye. Not only were all of the diffraction lines of Alpha iron present on the film, but these lines were wider than are obtained with ordinary grain size. The width of the lines was comparable to that obtained in x-ray crystallograms of such fine particles as colloidal gold. The x-ray affords a method of measuring grain size, in a qualitative way, and gives positive proof that the grains of the Alpha iron of martensite are very small. Bain estimates that the average diameter of the grains in martensite is about 100 to 200 atom diameters (approximately 0.000001 to 0.000002 in.). This figure is, of course, only an estimate, but it should be of the right order of magnitude.

Shape of Grains in Martensite.—It is not to be understood that the ferrite grains in martensite are necessarily equiaxed. The conditions obtaining during their formation are conducive to the formation of very small plates of ferrite running parallel to the cleavage planes of the austenite. Whether the grains are substantially equiaxed or in plates, their formation along the austenite cleavage planes gives rise to the acicular structure of martensite. The tendency for this cleavage precipitation is so marked that martensite formed by quenching large grains of austenite appears under low magnification to have a grain structure similar to that of the austenite. Detailed examination, however, reveals the fact that the austenite grain structure is entirely replaced by a structure so fine that it is often impossible to find a single crystalline particle large enough to be seen with a high-powered microscope. The apparent crystalline masses observed after light etching are seen to be, after deep etching, complexes of very fine structure.

Hardening Effect of Grain Refinement.—The hardening effect of grain refinement is shown in many metals and alloys and is well known. The most complete correlation of grain size and hardness is perhaps the work of Bassett and Davis¹ on Alpha brass. This alloy consists structurally of a single homogeneous solid solution, and is, therefore, comparable to a pure metal. Some typical values obtained in one series were:

¹ BASSETT, W. H. and DAVIS, C. H., "A Comparison of Grain Size Measurements and Brinell Hardness of Cartridge Brass," *Trans. Am. Inst. Mining Eng.*, vol. 60, p. 428.

AVERAGE GRAIN DIAMETER, INCHES	BRINELL HARDNESS
0.01400	41.7
0.00480	49.2
0.00300	52.4
0.00140	62.4
0.00093	77.4

The effect of moderate changes in grain size on hardness is relatively slight, and it may therefore seem somewhat strange to ascribe the great hardening effect in steel to grain refinement. The grain diameter of the second specimen in the above table

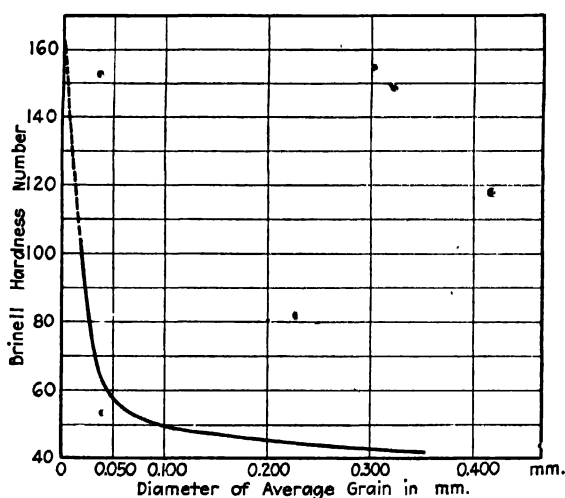


FIG. 190.—Relation between grain size and Brinell hardness in alpha brass. (Bassett and Davis.)⁴

is more than 50 per cent greater than the grain diameter of the third, whereas the hardness has only decreased about 6 per cent. The difference in grain size would be quite apparent under the microscope, while the difference in hardness is not very marked. Nevertheless, the total variation in hardness brought about by changes in grain size is quite considerable. The smallest grain size observed in brass by Bassett and Davis is large compared to the grain size which the authors believe to exist in martensite. It will be noted by referring to Fig. 190 that the hardness increases at a very rapid rate as the grains decrease in size below about 0.05 mm. diameter.

Rôle of Amorphous Iron.—Martensite is essentially crystalline. This is evident from *x*-ray and other information. Any amorphous iron present would be either at grain boundaries or at slip planes. The amount at slip planes would be slight, because the volume change when martensite forms is only 1.5 per cent. If amorphous iron is any considerable factor in the hardness of martensite, it must be the grain boundary amorphous iron.

Dissolved Carbon as a Cause of Hardening.—It has been stated by Le Chatelier, and the opinion is held by others, that martensite owes its hardness to carbon in solid solution in Alpha iron. The evidence given above is quite conclusive on the point that mildly tempered martensite contains very little carbon in solid solution, the bulk of it being precipitated as cementite. Such martensite is hard and the hardness cannot be due to carbon in solid solution. Great hardening can be produced in a steel containing 2 atoms per cent of carbon. No case is known where 2 atoms per cent of one element dissolved in a large-grained metal produces hardening at all comparable to that in the case of martensite containing 2 atoms per cent of carbon. In austenitic manganese steel, there may be as much as 7 atoms per cent carbon and 12 atoms per cent manganese dissolved in Gamma iron without producing any such marked hardening. The structure in this case is coarse-grained. It may be argued that 2 atoms per cent of carbon produce over 6 per cent of cementite and that it is this compound which is in solid solution in the ferrite. The same argument (though previously shown to be highly improbable) applies to manganese steel which would have more than 20 per cent cementite in solid solution.

It is probable that a given amount of carbon in atomic dispersion in Alpha iron would produce a greater hardening effect than in Gamma iron.¹ In order completely to account for the hardness of martensite in this manner, however, the hardening effect of carbon would have to be about 15 times as great in Alpha as its maximum possible effect in Gamma iron, as shown, for example, in austenitic manganese steel. According to this view, the addition of minute quantities of carbon (less than is soluble in Alpha iron at room temperature) to pure iron should produce a marked increase in hardness, which is not in accord with the facts.

¹ ROSENHAIN, "Solid Solutions," Lecture, February meeting of Am. Inst. Mining Eng., 1923.

Although some of the hardness of freshly formed martensite can be attributed to the atomic dispersion of carbon in Alpha iron, it seems to the authors that this is of secondary importance. In other words, if the Alpha iron containing the atomically dispersed carbon were coarse-grained, it is the authors' belief that it would be relatively soft. On the other hand, if the grains of pure Alpha iron could be made as small as the Alpha iron grains of high-carbon martensite, it is the opinion of the authors that relatively great hardness would result. Grain refinement is thus given as the most important cause of the hardness of freshly formed martensite, and the presence of carbon as a secondary cause.

Some Characteristics of Austenite.—A general effect of alloying elements, such as nickel, chromium, and manganese, is to facilitate the formation of martensite on quenching. That is, the cooling velocity required for the formation of martensite is less when these elements are present. Whereas a piece of carbon steel 1 in. in diameter will, when quenched in water, form an outer layer of martensite about $\frac{1}{8}$ in. thick and a martensite-troostite interior, a piece of alloy steel the same size will form martensite throughout under the same conditions.

The addition of these alloying elements also makes it easier to retain austenite at ordinary temperatures on quenching. The various kinds of austenite have different characteristics. The high-carbon (1.8), low-manganese (1.5) austenite can be transformed into martensite either by cooling in liquid air or by mild heating. Most of the varieties of room temperature austenite containing high carbon and a relatively small amount of other alloying element can be transformed to martensite by either cooling in liquid air or mild heating.

Hadfield's manganese steel (manganese about 12 per cent) when in the austenitic state is, however, very reluctant to transform to Alpha iron. The austenite is so stable that no ordinary heat treatment will cause its transformation. Mechanical work causes a partial transformation to martensite, with consequent increase in hardness. The transformation from Gamma to Alpha iron proceeds slowly at a temperature of 500 to 700° C. (932 to 1,292° F.). The austenite of manganese steel is greatly supersaturated with carbon at room temperature or at any temperature below 700° C. It appears that much carbide precipitation in this case precedes the Gamma to Alpha trans-

formation. The precipitation of carbide is apparently required to make the austenite less stable.

The precipitation of carbide from the austenitic manganese steel, without a simultaneous transformation of Gamma to Alpha iron, is quite analogous to the precipitation of the hard inter-metallic compounds in duralumin. It has been stated that austenitic manganese steel heated to 500° C. (932° F.) hardens much more rapidly than it increases in magnetism. Most of the hardness increase occurs before the specific magnetism has reached 2 per cent (pure iron equals 100 per cent) and before there is any marked change in the visible structure.¹

But manganese steel cannot be made very hard. The temperature at which the austenite transforms to martensite is such that grain growth of the ferrite can take place and the carbide particles will grow beyond the size for maximum hardness.

Structural Constituents in Steel.—It may be of interest to summarize the views given above regarding the nature of the various constituents occurring in steel.

Austenite.—A solid solution of carbon in Gamma iron. The iron atoms have the face-centered cubic arrangement. The carbon is atomically dispersed. The carbon atoms may be substituted for some of the iron atoms in the face-centered cubic lattice, or more probably occupy positions between the iron atoms. Austenite is relatively soft and ductile.

Martensite.—Very fine-grained Alpha iron containing carbon which, immediately after the formation of martensite, is atomically dispersed, but not in true or stable solid solution. The iron atoms have the body-centered cubic arrangement. On aging at room temperature, or more quickly on mild tempering, small particles of crystalline cementite form by the gradual diffusion of the carbon atoms and their association with iron atoms. The hardness of martensite increases with its carbon content and becomes very great at 0.70 per cent or more of carbon. At the same time ductility practically disappears. Martensite is formed from austenite on cooling at about 300° C. It is not a stable phase at any temperature.

Troostite.—An emulsion of very small cementite particles in fine-grained Alpha iron. It differs from martensite which has been aged or slightly tempered only in the larger size of the cementite particles and Alpha iron or ferrite grains. The size

¹ Horr, S. L., "Metals and the Common Alloys," pp. 347-349.

of both is still submicroscopic. Troostite is softer and more ductile than martensite of the same carbon content.

Troostite is formed (1) from austenite at about 600° C. on cooling at a rate too slow for the production of martensite but too fast for the production of sorbite, or (2) by reheating martensite to about 400° C. The troostites formed by these means differ both in appearance and in properties. Troostite is characterized by a very rapid etching rate.

Sorbite.—An emulsion of cementite particles in Alpha iron. The size of the cementite particles and of the Alpha iron grains is larger than in troostite, the cementite particles just approaching visibility under the microscope (diameter on the order of 0.00001 in.). Sorbite is softer and more ductile than troostite.

Sorbite may be formed on cooling austenite at a rate too slow for the production of troostite, or on reheating martensite or troostite to about 600° C. There is again a difference in appearance and properties according to the manner of formation.

Granular Pearlite.—Alpha iron containing the eutectoid percentage of carbon in the form of rounded cementite particles large enough to be seen. The diameter of the cementite particles is ordinarily on the order of 0.0001 in. The grain size of the Alpha iron is larger than in sorbite. Softer and more ductile than sorbite of the same carbon content.

Fundamental Distinctions.—From these definitions it will be seen that out of these five commonly recognized constituents there are only three fundamentally different types of structure:

1. Solid solution of carbon in Gamma iron—*austenite*.
2. Atomic dispersion of carbon in Alpha iron—*freshly formed martensite*.
3. Dispersion of cementite in Alpha iron—*aged or tempered martensite, troostite, sorbite, and pearlite*.

Further distinctions are of degree and not of kind.

High-speed Steel.—The most unique, and in many ways the most interesting, of the alloy steels is high-speed steel. A typical composition of high-speed steel is:

	PER CENT
Tungsten.....	18.0
Chromium	4.0
Vanadium.....	1.0
Carbon.....	0.7

These steels are termed "high-speed" because they retain cutting hardness at a dull red heat. The following general con-

siderations regarding high-speed steel are taken from Bain and Jeffries.¹

1. Ordinary high-speed steel contains sufficient carbon, tungsten, and chromium to be classed as a markedly hyper-eutectoid steel. There is a considerable amount of excess carbide at a temperature just above the A_{321} transformation. This fact is demonstrated clearly by microscopic examination. The atoms of the elements of high-speed steel are present in the ratio of about 84 iron, 6 tungsten, 6 chromium and vanadium together, and 4 carbon.

2. The excess carbide is more soluble in the austenitic matrix the higher the temperature.

3. The amount of alloying elements in ordinary high-speed steel is sufficient to form more carbide than is soluble even at incipient fusion of the steel.

4. At temperatures appreciably above the lower critical point, only one crystal structure in the carbide is present. This carbide is essentially an iron-tungsten carbide, but no doubt contains varying amounts of vanadium and chromium, with the retention of the same type of crystal structure. It is, of course, conceivable that, with certain chemical compositions, the carbon and tungsten would be present in such proportions that either of them might be substantially used up in the formation of the iron-tungsten carbide and leave an excess of the other element. In such a case it would be expected that an additional compound would form when conditions permitted. It is also submitted that the iron-tungsten carbide is the most stable carbide in high-speed steels above about 1,100° F. (595° C.).

5. As the iron-tungsten carbide dissolves in austenite at high temperatures, the constituents of the carbide, no doubt, are dissolved in the austenite as individual atoms. Before the quench, the high-speed steel consists of some residual, undissolved iron-tungsten carbide embedded in a matrix of austenite which contains a considerable proportion of the tungsten, carbon, chromium, and vanadium in solid solution.

6. The quenching of the high-speed steel leaves the residual carbide particles unchanged and produces varying amounts of martensite in accordance with the quenching temperature, and the remainder of the structure persists as austenite. Freshly

¹ "Cause of Red Hardness of High-speed Steel," *Iron Age*, p. 805, Sept. 27, 1923.

quenched high-speed steel, therefore, consists of a small amount of iron-tungsten carbide and the remainder is composed of martensite and austenite, in both of which the atoms other than iron are atomically dispersed. Grain growth in the austenitic matrix of high-speed steel at the quenching temperature is resisted by the presence of the residual carbide particles.

7. Some of the austenite, which exists at the high temperature, changes on quenching to martensite. The amount of austenite which remains unchanged increases with the temperature of the quench. This is probably due in part to the greater solubility of carbon, tungsten, and chromium in Gamma iron at higher temperatures—these elements acting to restrain the conversion.

8. In the martensite portion of the freshly quenched material, the only atoms which can migrate easily at room temperature or a little higher are the carbon atoms. In all probability the tungsten atoms are held in fixed positions in the iron lattice, and, likely, this is true also of chromium and vanadium. Iron atoms are available on every hand for combination with carbon atoms, and hence, even at room temperature, Fe_3C begins to form. The heat of formation of Fe_3C is probably the heat evolution observed by Brush in high speed steel.

9. At progressively higher temperatures, the chromium and vanadium will be capable of diffusion in the ferrite space lattice and carbides will form. The crystalline structure of the ferrite becomes more perfect and the carbide particles grow by coalescence to a super-critical size so as to soften the martensite at 850° F. (450° C.). The carbide precipitation in the order of availability of atoms accounts, in a large measure, for the softening, heat evolution, shrinkage, and magnetic point. The order of atomic volumes, from smallest to largest, of the principal elements involved is C, Fe, Cr, Va, W.

10. At about 850° F. (450° C.) the tungsten atoms are capable of slight diffusion, and at this temperature the formation of carbides will follow the order of carbide stability in preference to the sequence of atom availability. Iron-tungsten carbide is the most stable one and forms to the elimination of the earlier formed carbides.

11. The iron-tungsten carbide particles reach approximately the size for critical dispersion after a short reheat at 1,110° F. (595° C.). Within the grain growth temperature range, carbide particles are present to obstruct the growth and hence the grains

of the matrix are not permitted to grow excessively. The retention of small grains and the precipitation of the tungsten-iron carbide particles in critical size at 1,100° F. (595° C.) account for the red hardness in high-speed steel.

12. The austenite present after the quench may not undergo any change important to the physical properties of the steel up to the temperature of martensite transformation at from 850 to 1,100° F. (450 to 595° C.). Some excess cementite (Fe_3C) may precipitate from austenite below this temperature, but, if so, it would be regarded as only an incidental feature.

13. Between 850 and 1,110° F. (450 and 595° C.) the austenite transforms into martensite with expansion and increase in hardness. This hardness increase is termed "secondary hardening." At this temperature the iron-tungsten carbide can form, and does form, in critical dispersion. Its presence helps to keep the grain size of the new martensite small and to key the slip planes of the ferrite grains.

14. As the temperature is raised above 1,100° F. (595° C.) grain growth of the Alpha iron and particle growth of the iron-tungsten carbide produce rapid softening similar to the corresponding change in carbon steel at lower temperatures.

15. The double carbide contains its atoms in a relatively dense state. When double carbide dissolves in austenite the density of the steel is lowered, and when double carbide precipitates the density increases. There is also the usual decrease in density when austenite changes to martensite. This is largely due to the lower density of Alpha iron as compared to Gamma.

The cause of the red hardness of high-speed steel might be briefly stated as follows: The changes which cause martensite of carbon steel to soften are grain growth of the Alpha iron and growth of the carbide particles above critical size. Similar changes in high-speed steel take place only at a red heat. The outstanding reasons for the retention at red heat of fine grains in the ferrite of high-speed steel are the increased resistance to growth due to the elements in atomic dispersion in the ferrite and the copious presence of obstructing carbide particles. The reason for retention at red heat of carbide particles of critical size is the great stability of the iron-tungsten carbide and the large size of the tungsten atom. The great stability of this double carbide forces its formation to the exclusion or elimination of other carbides when the necessary atoms are available. The

large size of the tungsten atom prevents its diffusion in the ferrite space lattice until a temperature corresponding to a red heat is reached. The double carbide is an intermetallic compound which owes its existence entirely to crystallization. The formation of a particle of this carbide, therefore, requires a number of tungsten atoms which must be supplied by diffusion through the ferrite lattice. The precipitation and growth of the double carbide in quenched high-speed steel at a dull red heat are, therefore, somewhat comparable to the precipitation and growth of cementite in quenched carbon steel below 300° C.

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